

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 55728PCT5A	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/US 01/ 18502	International filing date (day/month/year) 08/06/2001	(Earliest) Priority Date (day/month/year) 29/06/2000
Applicant 3M INNOVATIVE PROPERTIES COMPANY		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 2 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

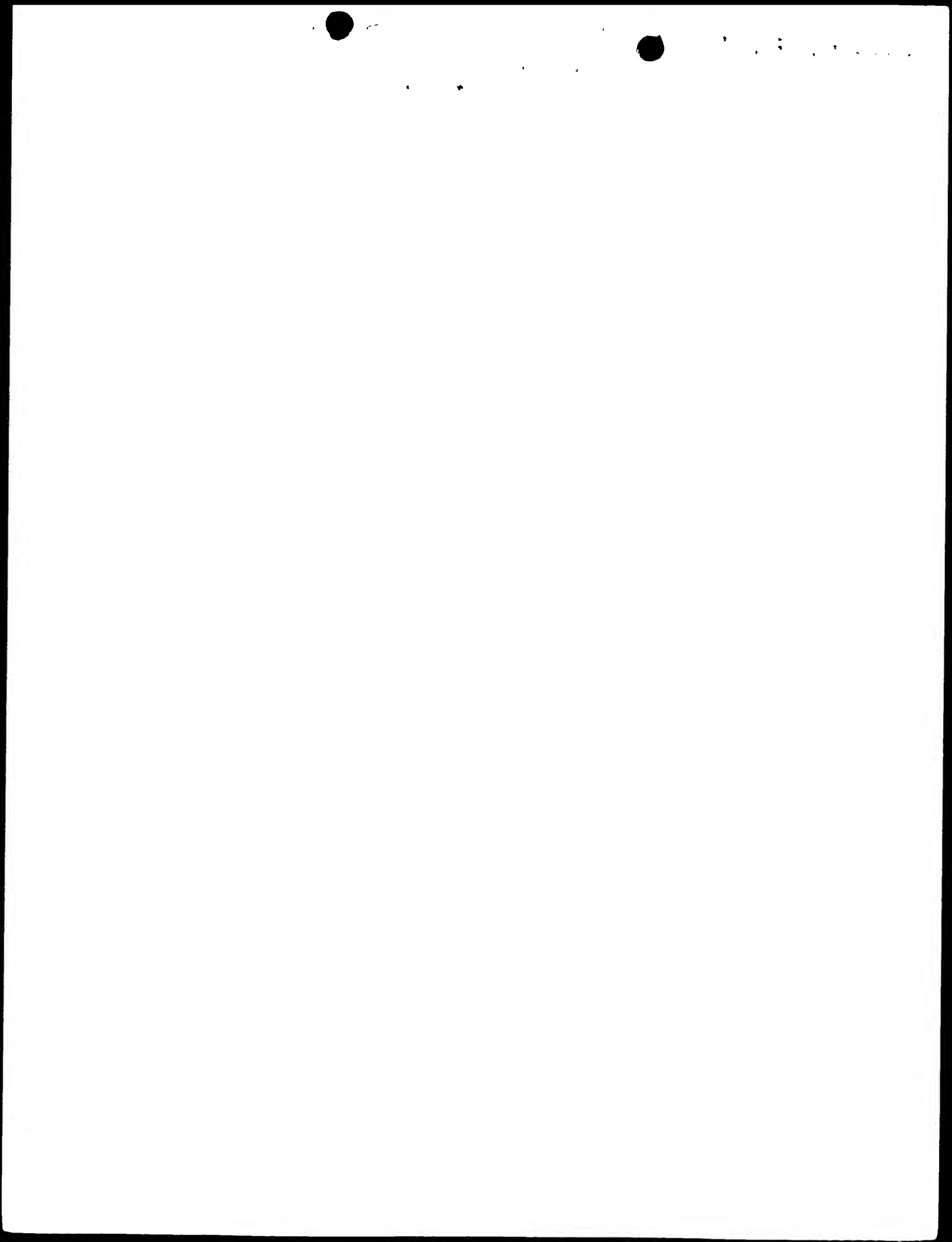
6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☐ None of the figures.



INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/18502

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08L27/12 C08K9/08 //(C08L27/12,91:00)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 948 830 A (MARTIN JON W ET AL) 14 August 1990 (1990-08-14) column 3; claims; table ---	1-26
A	WO 96 00761 A (DU PONT ;IER IND INC (US)) 11 January 1996 (1996-01-11) page 10, line 13-15; examples ---	1-26
A	US 3 929 707 A (BERG GERHARD ET AL) 30 December 1975 (1975-12-30) claims -----	1-26



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

28 September 2001

Date of mailing of the international search report

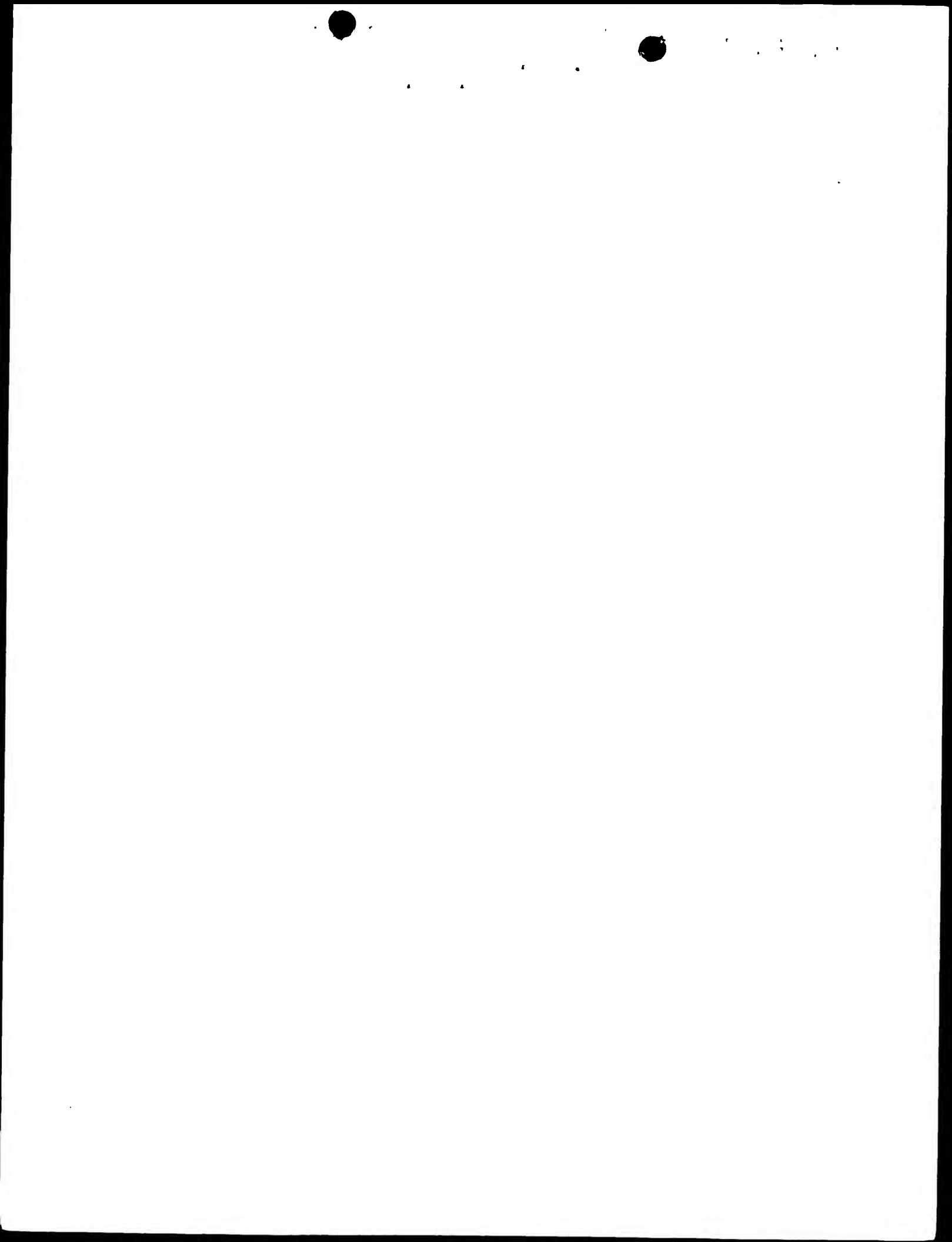
11/10/2001

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DE LOS ARCOS, E



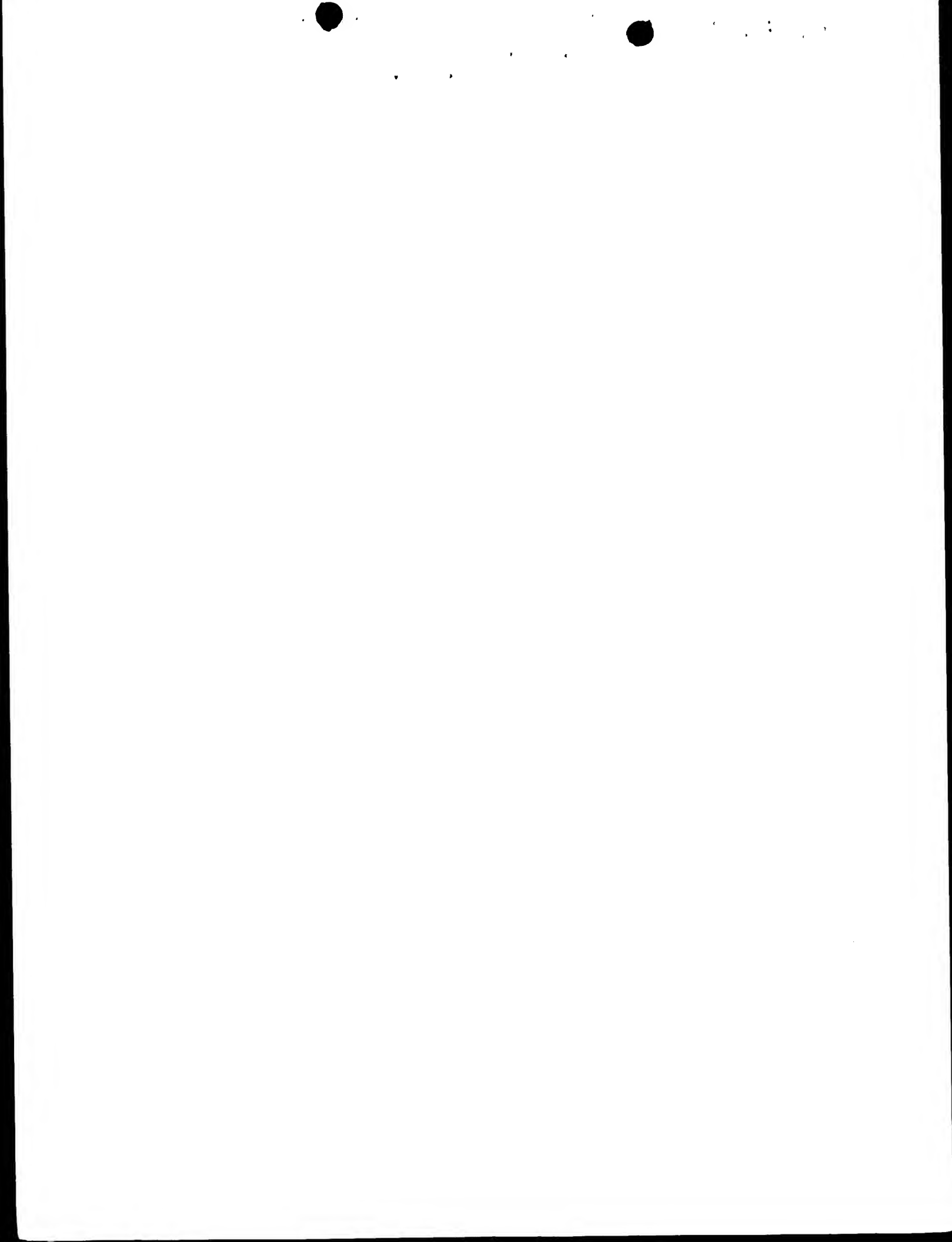
INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/18502

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4948830	A	14-08-1990	NONE	
WO 9600761	A	11-01-1996	US 5459202 A WO 9600761 A1	17-10-1995 11-01-1996
US 3929707	A	30-12-1975	DE 2332796 A1 AU 7054274 A BE 816976 A1 CA 1057878 A1 DD 111912 A5 FR 2235153 A1 GB 1464279 A IT 1016183 B JP 50043144 A JP 54004380 B NL 7406341 A SU 509244 A3	16-01-1975 08-01-1976 16-10-1974 03-07-1979 12-03-1975 24-01-1975 09-02-1977 30-05-1977 18-04-1975 06-03-1979 31-12-1974 30-03-1976



REC'D 29 MAY 2002

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

WIPO

PCT

(PCT Article 36 and Rule 70)


Applicant's or agent's file reference F 3059 PCT	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/US 01/ 18502	International filing date (day/month/year) 08/06/2001	Priority date (day/month/year) 29/06/2000
International Patent Classification (IPC) or national classification and IPC C08L27/12		
Applicant 3M INNOVATIVE PROPERTIES COMPANY et al.		

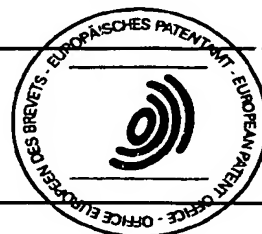
1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This **REPORT** consists of a total of 2 sheets, including this cover sheet.
- ☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

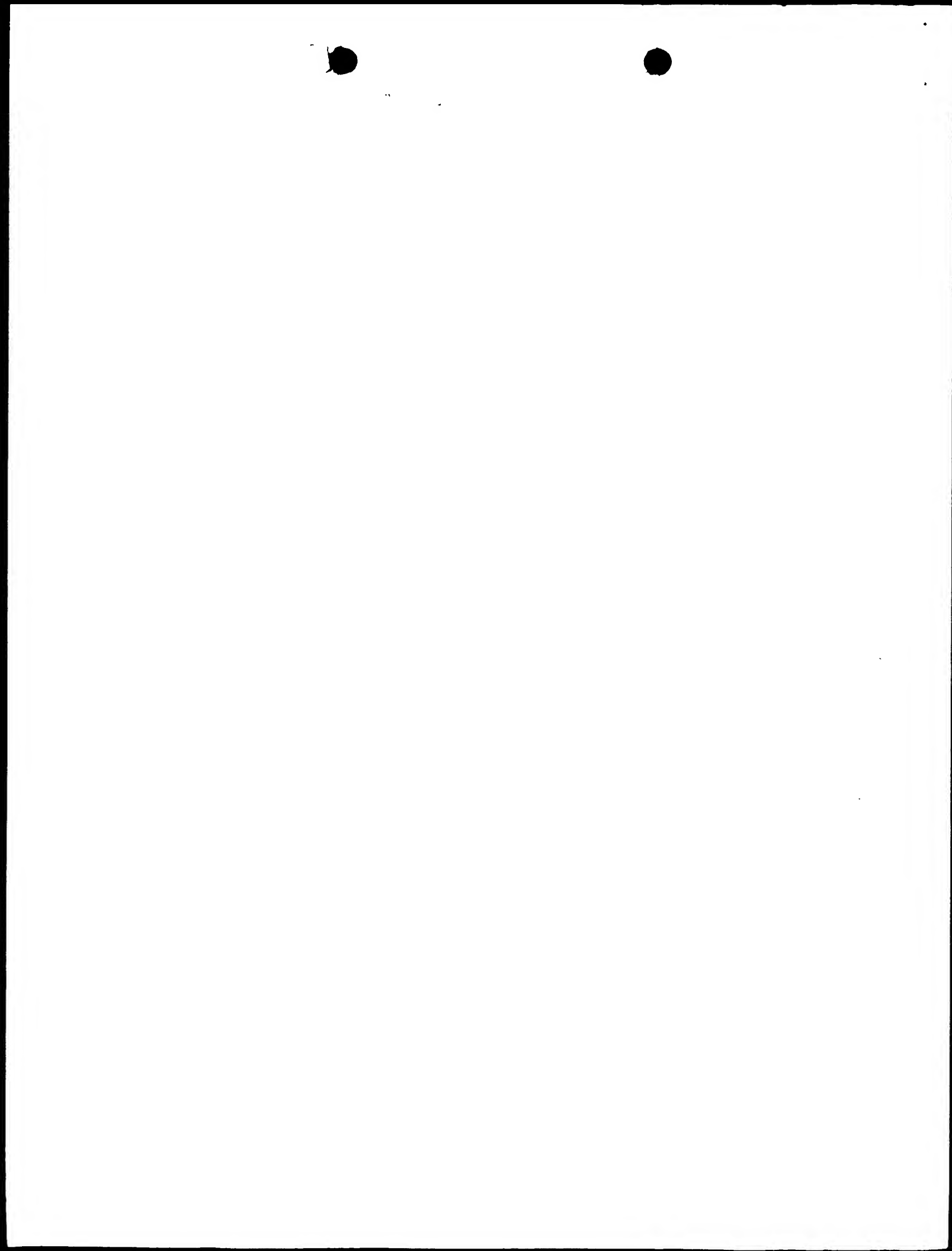
These annexes consists of a total of _____ sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 13/12/2001	Date of completion of this report 22/05/2002
Name and mailing address of the IPEA/  European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Netherlands Tel.: (+31-70) 340-2040 Fax: (+31-70) 340-3016	Authorized officer VAN THIELEN J B Tel. (+49-89) 2399 2828





I. Basis of the report

The basis of this international preliminary examination is the application as originally filed.

V. Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability

In light of the documents cited in the international search report, it is considered that the invention as defined in at least some of the claims does not appear to meet the criteria mentioned in Article 33(1) PCT, i.e. does not appear to be novel and/or to involve an inventive step (see international search report, in particular the documents cited X and/or Y and corresponding claim references).

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
10 January 2002 (10.01.2002)

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(10) International Publication Number
WO 02/02690 A1

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- (21) International Application Number: **PCT/US01/18502**
- (22) International Filing Date: **8 June 2001 (08.06.2001)**
- (25) Filing Language: **English**
- (26) Publication Language: **English**
- (30) Priority Data:
00202277.0 **29 June 2000 (29.06.2000)** **EP**
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- (74) Agents: **LILLY, James, V.** et al.; Office of Intellectual Property Counsel, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AT (utility model), AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, CZ (utility model), DE, DE (utility model), DK, DK (utility model), DM, DZ, EC, EE, EE (utility model), ES, FI, FI (utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (utility model), SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:**
— *with international search report*
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: **FLUROELASTOMER COMPOSITION COMPRISING A MINERAL OIL**

(57) Abstract: The present invention provides the use of a mineral oil in a fluoroelastomer composition comprising a fluoroelastomer to improve the flow of said composition during processing to form an article therefrom and/or to improve the release from a mold of a vulcanized article produced from said fluoroelastomer composition. Further provide are a fluoroelastomer composition that includes a mineral oil, a method of making an article therewith and a method of preparing the fluoroelastomer composition.

WO 02/02690 A1



FLUOROELASTOMER COMPOSITION COMPRISING A MINERAL OIL

1. Field of the invention

The present invention relates to fluoroelastomer compositions that show an improved flow when being processed to an article by means of for example extrusion or injection molding. The invention further relates to a method of making such fluoroelastomer composition and to a method of making articles using such a fluoroelastomer composition.

2. Background of the invention.

Fluoroelastomers, particularly the copolymers of vinylidene fluoride with other ethylenically unsaturated halogenated monomers, such as hexafluoropropene, have particular utility in high temperature applications, such as seals, gaskets, and linings--see, for example, Brullo, R. A., "Fluoroelastomer Rubber for Automotive Applications," Automotive Elastomer & Design, June 1985, "Fluoroelastomer Seal Up Automotive Future," Materials Engineering, October 1988, and "Fluorocarbon Elastomers," Kirk-Othmer, Encyclopedia of Chemical Technology, Vol. 8, pp. 990-1005 (4th. ed., John Wiley & Sons, 1993).

Fluoroelastomers when cured have good resistance to damage by heat, solvents, corrosive chemicals, and steam. However, in the manufacture of molded products from these polymers, particularly in modern manufacturing methods, e.g., injection molding, the cured polymers generally adhere to the surface of the mold even when mold release agents are sprayed on the mold cavity or incorporated in the polymer, and the shaped article is frequently torn or damaged when removed from the mold. Also, the incorporation of a mold release agent into the polymer can have serious adverse effects on the physical properties of the cured composition, for example, Mooney Scorch and compression set, which can limit the successful commercial use of the cured composition. Deposits of polymer on the mold cavity surface ("mold fouling") and poor release of the shaped vulcanizate from the mold are major reasons for defects, resulting in rejection of the shaped article which adds to the expense of manufacture of such molded articles.

Furthermore, the processability in terms of ease of mixing, moulding cycle times and throughput in case of extrusion is fairly poor compared to conventional elastomers because of the poor flow characteristics of the fluoroelastomer during processing. Processing aids have been suggested to improve the processability of fluoroelastomers such as for example disclosed in EP 691 371.



However, although such processing aids are effective, there continues to exist a need to find further suitable processing aids. However, such processing aids should not adversely affect the properties of the fluoroelastomer article produced and should desirably be compatible with existing manufacturing procedures, in particular, they preferably should not contaminate the equipment or contribute to flow defects, such as knit-lines. Furthermore, the processing aids should desirably not affect the scorching safety or preferably improve the scorching safety.

Knit-lines are molding defects resulting from the incomplete joining of two or more polymer streams during the molding process. While changing the mold temperature or compound temperature may influence this behavior, incompatible process aids may have a larger effect. To the extent any process aid or additive exudes to the surface of the molten polymer stream during processing, such a layer of exuded process aid or additive may serve to prevent the proper joining or knitting of the two molten polymer streams as they meet in a mold cavity. This incomplete or defective joining of the polymer streams results in a defect in the finished part called a knit-line and is a likely point of failure in use.

Many conventional fluoroelastomer compositions tend toward "scorching" behavior, i.e., the premature crosslinking or partial cure of the composition when exposed to elevated temperatures or conditions of high shear. This scorching behavior particularly is pronounced when the fluoroelastomer is injection molded, wherein scorching is characterized by a premature cure initiation occurring prior to and during injection of the compounded composition into a mold. The point of cure initiation for injection-molded fluoroelastomers may be defined as the time after which the compounded fluoroelastomer is subjected to injection molding conditions (i.e., upon introduction into an injection barrel at a temperature above approximately 70-90° C. and/or while injecting the compound into the mold under high shear at temperatures between about 180 and 200° C.) when the curing compound begins to gel or harden. Such a change in physical properties, particularly the corresponding viscosity increase, can greatly reduce processing efficiency by hindering the ability to inject the compounded mixture into a mold. Scorching phenomena also produce high levels of waste product; because a cured fluoroelastomer is very difficult to reprocess, any fluoroelastomer that cures outside the mold cavity must usually be discarded.



3. Summary of the invention

It has been found that the addition of a mineral oil to a fluoroelastomer composition improves the flow of the composition when that composition is being processed to form an article. In particular, it has been found that the throughput of the composition in extrusion is substantially improved by the mineral oil. Also, the speed of mold filling and the flow path length of the composition in injection molding, transfer molding and compression molding can be improved by the mineral oil. When forming certain articles such as O-rings, a knit-line, which might be formed at the point where the composition flows meet, can generally be avoided with the aid of the mineral oil. It has also been observed that articles produced from a fluoroelastomer composition that includes a mineral oil generally have an improved release from a mold after vulcanization leading to decreased mold defects. Finally, the mineral oil addition does not adversely affect scorching.

The present invention thus provides the use of a mineral oil in a fluoroelastomer composition comprising a fluoroelastomer to improve the flow of said composition during processing to form an article therefrom and/or to improve the release from a mold of a vulcanized article produced from said fluoroelastomer composition.

In a further aspect of the present invention, there is provided a method of making a fluoroelastomer article comprising the steps of providing a fluoroelastomer composition comprising a fluoroelastomer and a mineral oil and processing said composition to form said fluoroelastomer article by means of a processing technique selected from the group consisting of extrusion, injection molding, transfer molding, compression molding and combinations thereof.

The invention also provides a fluoroelastomer composition comprising a fluoroelastomer and a mineral oil, said composition being free of vegetable wax or containing vegetable wax in an amount of less than 2 parts by weight per 100 parts by weight of fluoroelastomer.

Finally, the invention provides a method of making a fluoroelastomer composition having improved flow characteristics when processed, said method comprising the steps of blending together a mineral oil and a fluoroelastomer to obtain a fluoroelastomer composition that is free of vegetable wax or alternatively to blend together a mineral oil, a fluoroelastomer and a



vegetable wax to obtain a fluoroelastomer composition that contains a vegetable wax in an amount of less than 2 parts by weight for 100 parts by weight of fluoroelastomer.

4. Detailed description of the invention

- 5 The mineral oils used in the fluoroelastomer composition may comprise naphthenic, aromatic (other than naphthenic) and paraffinic hydrocarbons and mixtures thereof. Mineral oils have been classified by their content of naphthenic, aromatic and paraffinic content into 4 major categories according to ASTM norm D-2226-93. These categories include 101 (highly aromatic), 102 (aromatic), 103 (naphthenic) and 104 (paraffinic). Any mineral oil can be used
10 with the fluoroelastomer composition although the mineral oils belonging to the categories 102, 103 and 104 are generally preferred. The amount of mineral oil contained in the composition may vary over a broad range but will generally be between 0.25 parts by weight and 15 parts by weight per 100 parts by weight of the fluoroelastomer. If the amount of mineral oil is below 0.25 parts, the effect of the mineral oil on the flow properties of the fluoroelastomer during
15 processing may be too small or practically absent whereas an amount above 15 parts by weight may negatively impact the desired end properties of the fluoroelastomer article produced from the composition. A preferred range of mineral oil is between 0.5 parts by weight and 8 parts by weight per 100 parts by weight of the fluoroelastomer.
- 20 As is well known to those skilled in the art, mineral oils are incompatible with fluoroelastomers ("Modern Fluoropolymers", Edited by John Scheirs, 1997, John Wiley & Sons Ltd., chapter 5 and 32). For this reason, the oils have been avoided because they could disrupt the mixing process by which the fluoroelastomer is blended with other components. It has nevertheless been found in the present invention that the mineral oil can be blended with the fluoroelastomers
25 when the oil is very slowly mixed into the fluoroelastomer. However, a more commercially attractive way to include the mineral oil into the composition comprises adsorbing the mineral oil on a carrier prior to mixing with the fluoroelastomer. Suitable carriers are generally solid carriers capable of adsorbing the oil. Typically, suitable carriers comprise carbon black or inorganic particles such as silicates, barium sulfate, clays, carbonates, calcium hydroxide, oxides
30 like calcium oxide, magnesium oxide, chromium oxide, iron oxides and titanium oxide. To load the mineral oil on the carrier, the carrier is mixed with the mineral oil so as to adsorb the mineral oil. It is commercially most attractive that the carrier is fully saturated with the mineral oil, i.e. the oil is added to the carrier until no further oil is adsorbed by it. The mineral oil adsorbed on



the carrier, for example oil adsorbed on carbon black or inorganic particles can then be easily blended into the fluoroelastomer. It is believed that during this blending operation at least some of the oil will desorb from the carrier for example under the influence of heat and kinetic energy supplied to the composition while mixing.

5

In a particular aspect of the present invention, the fluoroelastomer composition may further comprise a vegetable wax or non-vegetable wax and derivatives thereof such as Armeen™ 18D. A synergistic effect on the flow properties of the fluoroelastomer composition during processing has been observed if the mineral oil is used in combination with a wax. For example, good flow properties were obtained with 2 parts or less by weight of mineral oil per 100 parts by weight of fluoroelastomer combined with 1 part by weight or less of a wax, in particular a vegetable wax, per 100 parts by weight of fluoroelastomer. Preferably, the amount of wax (vegetable or non-vegetable) included in the fluoroelastomer composition will be less than 2 parts by weight per 100 parts by weight of the fluoroelastomer. Particularly when the wax is a vegetable wax, the amount thereof is preferably kept below 2 parts by weight per 100 parts by weight of fluoroelastomer, preferably between 0.2 and 1.5 parts by weight for 100 parts by weight of fluoroelastomer. It has been observed that if the amount of vegetable wax such as carnauba wax is included in amounts of 2 or more parts by weight per 100 parts by weight of the fluoroelastomer, the composition may become undesirable for processing with injection molding and extrusion and /or have an undesirable effect on the properties of the finished article. Examples of waxes that may be used in the fluoroelastomer composition include carnauba wax, VPA No. 2, Montan wax, polyethylene wax.

The fluoroelastomer contained in the fluoroelastomer compositions according to the invention is generally a polymer that has elastomeric properties and that comprises a major portion of repeating units that are derived from an ethylenically unsaturated and fluorinated monomer, such as an ethylenically unsaturated monomer having a fluorinated double bond (i.e. one or more of the carbon atoms of the double bond carry one or more fluorine atoms). Fluoroelastomers in connection with the present invention include perfluoroelastomers as well as elastomers that are not fully fluorinated. Preferred fluoroelastomers are polymers that have repeating units derived from one or more of the following fluoromonomers: vinylidene fluoride (VF2), hexafluoropropene (HFP), chlorotrifluoroethylene, 2-chloropentafluoropropene, fluorinated vinyl ethers such as perfluoro(methyl vinyl ether) (PMVE), fluorinated allyl ethers,



tetrafluoroethylene (TFE), 1-hydropentafluoropropene, dichlorodifluoroethylene, trifluoroethylene, and mixtures thereof. The aforementioned fluoromonomers may further be copolymerized with other compounds such as with cure-site monomers (CSM) (e.g. bromine containing monomers or perfluorinated monomers such as perfluorobenzyl vinyl ether) or with
5 non-fluorinated alpha olefin co-monomers such as ethylene (E) and propylene (P). Preferred elastomers are copolymers of vinylidene fluoride and at least one terminally ethylenically-unsaturated fluoromonomer containing at least one fluorine atom substituent on each double-bonded carbon atom, each carbon atom of said fluoromonomer being substituted only with
10 fluoroalkoxy radical. Specific examples of copolymers include copolymers having a combination of monomers as follows: VF2-HFP, VF2-TFE-HFP, VF2-TFE-HFP-CSM, VF2-TFE-PMVE-CSM, TFE-P, E-TFE-PMVE-CSM and TFE-PMVE-CSM.

Fluoroelastomer copolymers according to the type described above are available commercially
15 as copolymer gumstock under for example the "Dyneon" trademark by Dyneon LLC of Saint Paul, Minn. Suitable products of this line include Dyneon™ FC-2230, FC-2145, FC-2178, and FC-2211. Other commercially available products include fluoroelastomers sold under the "Viton" trademark.

20 The fluoroelastomer compositions further typically include a cure system, also called vulcanization system so as to provide the capability of vulcanization to the fluoroelastomer compositions. Suitable curing systems for use in the compositions include the curing systems known in the prior art. Useful curing systems include for example the peroxide curing system and the polyhydroxy curing system. The polyhydroxy curing system generally comprises one or
25 more polyhydroxy compounds and one or more organo-onium accelerators. The organo-onium compounds useful in the present invention typically contain at least one heteroatom, i.e., a non-carbon atom such as N, P, S, O, bonded to organic or inorganic moieties. One class of quaternary organo-onium compounds useful in the present invention broadly comprises relatively positive and relatively negative ions wherein a phosphorus, arsenic, antimony or
30 nitrogen generally comprises the central atom of the positive ion, and the negative ion may be an organic or inorganic anion (e.g., halide, sulfate, acetate, phosphate, phosphonate, hydroxide, alkoxide, phenoxide, bisphenoxide, etc.).



Many of the organo-onium compounds useful in this invention are described and known in the art. See, for example, U.S. Pat. Nos. 4,233,421 (Worm), 4,912,171 (Grootaert et al.), 5,086,123 (Guenthner et al.), and 5,262,490 (Kolb et al.), US 5,929,169, all of whose descriptions are herein incorporated by reference. Representative examples include the following individually

5 listed compounds and mixtures thereof:

triphenylbenzyl phosphonium chloride

tributylallyl phosphonium chloride

tributylbenzyl ammonium chloride

tetrabutyl ammonium bromide

10 triaryl sulfonium chloride

8-benzyl-1,8-diazabicyclo [5,4,0]-7-undecenium chloride

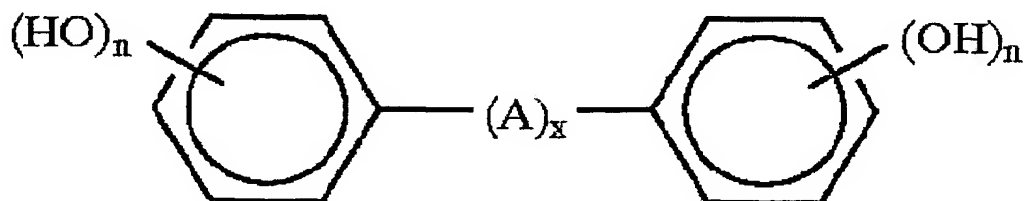
benzyl tris(dimethylamino) phosphonium chloride

benzyl(diethylamino)diphenylphosphonium chloride

Another class of useful organo-onium compounds include those having one or more pendent

15 fluorinated alkyl groups. Generally, the most useful fluorinated onium compounds are disclosed by Coggio et al. in U.S. Pat. No. 5,591,804.

The polyhydroxy compound may be used in its free or non-salt form or as the anionic portion of a chosen organo-onium accelerator. The crosslinking agent may be any of those polyhydroxy
20 compounds known in the art to function as a crosslinking agent or co-curative for fluoroelastomers, such as those polyhydroxy compounds disclosed in U.S. Pat. Nos. 3,876,654 (Pattison), and 4,233,421 (Worm). Representative aromatic polyhydroxy compounds include any one of the following: di-, tri-, and tetrahydroxybenzenes, naphthalenes, and anthracenes, and bisphenols of the following formula:





- wherein A is a difunctional aliphatic, cycloaliphatic, or aromatic radical of 1 to 13 carbon atoms, or a thio, oxy, carbonyl, sulfonyl, or sulfonyl radical, A is optionally substituted with at least one chlorine or fluorine atom, x is 0 or 1, n is 1 or 2, and any aromatic ring of the polyhydroxy compound is optionally substituted with at least one atom of chlorine, fluorine, bromine, or with a carboxyl or an acyl radical (e.g., --COR where R is H or a C1 to C8 alkyl, aryl, or cycloalkyl group) or alkyl radical with, for example, 1 to 8 carbon atoms. It will be understood from the above bisphenol formula that the --OH groups can be attached in any position (other than number one) in either ring. Blends of two or more of these compounds are also used.
- 10 One of the most useful and commonly employed aromatic polyphenols of the above formula is 4,4'-hexafluoroisopropylidene bisphenol, known more commonly as bisphenol AF. The compounds 4,4'-dihydroxydiphenyl sulfone (also known as Bisphenol S) and 4,4'-isopropylidene bisphenol (also known as bisphenol A) are also widely used in practice.
- 15 Prior to curing, an acid acceptor is mixed into a fluoroelastomer composition that comprises a polyhydroxy cure system, after which storage life of the composition is more limited. Acid acceptors can be inorganic or blends of inorganic and organic. Examples of inorganic acceptors include magnesium oxide, lead oxide, calcium oxide, calcium hydroxide, dibasic lead phosphite, zinc oxide, barium carbonate, strontium hydroxide, calcium carbonate, etc. Organic acceptors
- 20 include epoxies, sodium stearate, and magnesium oxalate. The preferred acid acceptors are magnesium oxide and calcium hydroxide. The acid acceptors can be used singly or in combination, and preferably are used in amounts ranging from about 2 to 25 parts per 100 parts by weight of the fluoroelastomer.
- 25 The peroxide cure system may also be used to provide vulcanization capability to the fluoroelastomer composition. In case of a peroxide cure system, the fluoroelastomer should comprise a cure site component that is capable of participating in a peroxide cure reaction. The peroxide cure system further comprises a peroxide curative and optionally one or more co-agent that also participate in the peroxide cure reaction. The cure site component contained in the
- 30 fluoroelastomer is generally a halogen containing material that is capable of participation in a peroxide cure reaction. Typically the halogen is bromine or iodine. Suitable cure-site components include terminally unsaturated monoolefins of 2 to 4 carbon atoms such as bromodifluoroethylene, bromotrifluoroethylene, iodotrifluoroethylene, and 4-bromo-3,3,4,4-



tetrafluorobutene-1. Examples of other suitable cure site components include $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{Br}$, $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{CF}_2\text{Br}$, and $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{Br}$. Preferably, all or essentially all of these components are ethylenically unsaturated monomers.

- 5 Other useful cure-site components are brominated or iodinated chain transfer agents and initiators. Examples of useful chain transfer agents include perfluoroalkyl bromides or iodides. Examples of useful initiators include $\text{NaO}_2\text{SC}_2\text{F}_4\text{OF}_4\text{X}$ (where X is Br or I). Suitable peroxide curatives are those which generate free radicals at curing temperatures. A dialkyl peroxide or a bis(dialkyl peroxide) which decomposes at a temperature above 50°C is especially preferred. In many cases it is preferred to use a di-tertiarybutyl peroxide having a tertiary carbon atom attached to peroxy oxygen. Among the most useful peroxides of this type are 2,5-dimethyl-2,5-di(tertiarybutylperoxy)hexyne-3 and 2,5-dimethyl-2,5-di(tertiarybutylperoxy)hexane. Other peroxides can be selected from such compounds as dicumyl peroxide, dibenzoyl peroxide, tertiarybutyl perbenzoate, α,α' -bis(t-butylperoxy-diisopropylbenzene), and di[1,3-dimethyl-3-(t-butylperoxy)-butyl]carbonate. Generally, about 1-3 parts by weight of peroxide per 100 parts by weight of fluoroelastomer is used.

- Another material which is usually blended with the composition as a part of the peroxide curative system is a coagent composed of a polyunsaturated compound which is capable of cooperating with the peroxide to provide a useful cure. These coagents can be added in an amount equal to 0.1 and 10 parts per hundred parts by weight of fluoroelastomer, preferably between 2-5 parts per hundred parts by weight of fluoroelastomer. Examples of useful coagents include triallyl cyanurate; triallyl isocyanurate; tri(methylallyl isocyanurate); tris(diallylamine)-s-triazine; triallyl phosphite; N,N-diallyl acrylamide; hexaallyl phosphoramidate; N,N,N',N'-tetraalkyl tetraphthalamide; N,N,N',N'-tetraallyl malonamide; trivinyl isocyanurate; 2,4,6-trivinyl methyltrisiloxane; and tri(5-norbornene-2-methylene)cyanurate. Particularly useful is triallyl isocyanurate.

Other useful coagents include the bis-olefins disclosed in EPA 0 661 304 A1, EPA 0 784 064 A1 and EPA 0 769 521 A1.

30

The fluoroelastomer composition may include further additives which are commonly used in the art such as fillers and processing aids commonly used in fluoroelastomer compositions. Fillers are usually included in an amount of up to 100 parts by weight for 100 parts by weight of



fluoroelastomer, preferably in an amount of 1 to 50 parts by weight for 100 parts by weight of fluoroelastomer. Examples of fillers include thermal grade carbon black or non-black pigments of relatively low reinforcement characteristics such as clays or barytes. Diorgano sulfur oxide compounds may be added as well as other ingredients such as retarding agents and processing
5 aids such as for example Structol™ WS 280.

To prepare the fluoroelastomer composition, the fluoroelastomer or mixture of fluoroelastomers, mineral oil preferably loaded on a carrier, vulcanization components and further optional adjuvants are intimately mixed by employing any of the known rubber mixing devices such as
10 Banbury mixers, roll mills or any other convenient mixing device. For best results, the temperature of the composition during mixing should not rise above 120°C.

The fluoroelastomer compositions can be used to form articles. By the term "article" in connection with the present invention is meant a final article such as for example an O-ring as
15 well as preforms from which a final shape is made, e.g. a tube from which a ring is cut. To form an article, the fluoroelastomer composition can be extruded using a screw type extruder or a piston extruder. Alternatively, the fluoroelastomer composition can be shaped into an article using injection molding, transfer molding or compression molding. Compression molding consists of placing a quantity of cold uncured elastomer mixture into a heated mold cavity and
20 subsequently closing the mold using adequate pressure to shape the article. After retaining the rubber at sufficient temperature during sufficient time to allow vulcanization to proceed it can then be demolded. Injection molding is a shaping technique whereby the elastomer mixture is first heated and masticated in an extruder screw then collected in a heated chamber from which it is then injected into a hollow mold cavity by means of a hydraulic piston. After vulcanization
25 the article can then be demolded. Transfer molding is similar to injection molding with the difference being that the elastomer mixture is not preheated and masticated by an extruder screw but introduced as a cold mass in the heated injection chamber.

Typical vulcanization conditions for fluoroelastomer mixtures are elevated temperatures e.g. 160°C to 210°C, pressures above 7 bar and maintaining these conditions for 30 seconds, in fast
30 injection molding processes to 5 minutes or longer for larger compression molded articles.

The following examples illustrate the invention further without however the intention to limit the invention thereto.



EXAMPLES

Abbreviations

Ex : example

- 5 Oiled black : Multiblack™ : carbon black containing 50% oil (8% aromatic, 27% naphthenic, 65% paraffinic oil), available from Multiblend Chemicals Limited, Manchester.
MT N-990 : Huber™ N 990 MT : carbon black, available from Degussa
Ca(OH)₂ : calcium hydroxide, Rhenofit CF available from RheinChemie.
Carnauba wax : Flora™ 202, available from Int. Wax & Refining Co
- 10 Struktol™ WS-280 : Organic silicone derivative, available from Schill & Seilacher
Armeen™ 18D : Octadecylamine, available from Akzo-Nobel
MgO : magnesium oxide : Elastomag™ 170 PWD, available from Morton International
PennzUltra™ 1122 and 1199 : Paraffinic rubber oils, available from Pennzoil-Quaker State Company
- 15 PennzNap™ 60, 500 and 1500 : Naphthenic Rubber oils, available from Pennzoil-Quaker State Company
Saltex™ : Aromatic extract, available from Pennzoil-Quaker State Company
FC-2174 : vinylidene fluoride, hexafluoropropylene copolymer with incorporated cure system, available from Dyneon
- 20 FC-2176: vinylidene fluoride, hexafluoropropylene copolymer with incorporated cure system, available from Dyneon
FC-2181: vinylidene fluoride, hexafluoropropylene copolymer with incorporated cure system, available from Dyneon
E-14251 A: vinylidene fluoride, hexafluoropropylene, tetrafluoroethylene copolymer with
- 25 incorporated cure system, available from Dyneon
E-15948: vinylidene fluoride hexafluoropropylene copolymer with incorporated cure system, available from Dyneon
FE 5840Q: vinylidene fluoride, hexafluoropropylene, tetrafluoroethylene copolymer with incorporated cure system, available from Dyneon
- 30 BRE-7132X : Vinylidene fluoride, propylene, tetrafluoroethylene copolymer with incorporated cure system, available from Dyneon



Test methods

Cure and rheological properties of fluoroelastomer compositions were evaluated using the following test methods:

Vulcanisation behaviour Tests were run on uncured, compounded admixtures using the Goettfert

- 5 Moving Die Rheometer (MDR) at 180 deg. C. on an 8 g quantity of the admixture in accordance with ASTM D 5289-93a for a rotorless curemeter, no preheat, an oscillator frequency of 50 cpm and a 0.2 deg. arc. Minimum torque (ML), maximum torque (MH), and the difference between MH and ML (delta torque), were reported. Also reported were Ts2 (the time to a 2 unit rise in torque from ML ; Tc50 (the time to increase torque above ML by 50% of delta torque), and
- 10 Tc90 (the time to increase torque above ML by 90% of delta torque), all of which were reported in minutes. The maximum attainable vulcanization speed was represented by VMAX (Nm/min).

- Mooney Scorch was measured according to ASTM 1664, Part C (Measuring pre-vulcanisation characteristics). The minimum viscosity (Mmin) was recorded, as well as T3 (time to scorch =
- 15 Mmin + 3 units) and T18 (time to cure : Mmin + 18 units).

Press-Cure data are data obtained from mechanical property testing after 150 by 150 by 2 mm sheets were pressed and allowed to vulcanise for 7 minutes at 177°C mold temperature.

- Post-Cure data was obtained from sheets prepared as described above which were then further treated by heating the sheets in a circulating air oven maintained at about 230 deg. C. for 16
- 20 hours.

- Tensile Strength at Break, Elongation at Break and Stress at 100% Elongation were determined using a Instron™ mechanical tester with a 1kN load cell in accordance with ASTM D 412-92. Test specimen strips were cut from the press- or post-cured sheets. All tests were run at a constant cross head displacement rate of 500 mm/min. in fivefold. The values reported were
- 25 averages of the five tests. Hardness Shore A (2"), Stress at 100% Elongation, Elongation at Break, and Tensile Strength at Break were reported in units of Mega Pascals (MPa), %, and MPa respectively.

- Compression set resistance was measured on buttons, according to ASTM D395 (method B (25% deformation)). The buttons were molded at 177°C for 15 minutes and subsequently post
- 30 cured for 16 hrs at 230°C.

Internal Diameter (ID) measurement on O-rings was done using a Mitutoyo™ measuring projector.



The rheological behaviour of the fluoroelastomer compound was evaluated by using a Rheovulkameter, available from Goettfert, using a spiral mold.

The Rheovulkameter can be further characterised by the following parameters : temperature of the die and the piston were 100 deg. C, the temperature of the mold was 180 deg. C. The hydraulic pressure used was 80 bar. A preheat of 50 seconds and injection time of 120 seconds was used. After that the compound mixture was allowed to vulcanise for 3 minutes . The total volume (mm^3) and the maximum volume per second (mm^3/s) were recorded.

Evaluations of injection molding performance, i.e. mold release and flow under injection molding conditions, were performed using a DESMA 966.053 ZO lab injection molding machine available from Kloeckner Ferromatic Desma GmbH of Germany. The machine is further described as having 500 kN mold closing force, 27 kW total power installed, 55 mm injection piston diameter, 120 mm maximum piston stroke, 200 Mpa maximum injection pressure, 400 mm/sec. maximum injection speed and a plastication unit with 30 mm screw diameter and screw RPM of 30-220.

Two molds were used for the experiments : an O-ring mold and a spiral mold.

The O-ring mold was a 4 cavity mold with O-ring cavity internal diameter of 49.5 mm, O-ring cross-section of 3.00 mm, a runner length of 13 mm, sprue base diameter of 5.2 mm, sprue length of 29 mm, and each cavity had a vacuum canal. The mold steel was STAVAX ESR™ with a surface finish EDM.

Multiple molding cycles were made of each tested mixture.

The steady state O-ring injection molding conditions were 190 deg. C. mold temperature, 95 deg. C. injection barrel temperature, 60 deg. C. screw barrel temperature, injection speed 60% of maximum, after-injection pressure of 4.0 MPa for 5 seconds, screw RPM 35% of maximum, and a vacuum time of 2.5 seconds. The holding time and heating time were both dependent upon vulcanization speed and were adjusted to obtain cured O-rings. The injection volume was adjusted to give similar flash to the parts molded.

The second mold used was a spiral mold :

The spiral was 1000 mm long, 1.2 mm deep and 5 mm wide. The flow speed was followed by means of pressure sensors at 100 mm and at 200 mm. The time to reach 100 mm and 200 mm was recorded. Also the ultimate flow length of each mixture was recorded. This value was obtained by taking the average measured length of 10 molded spirals collected after first molding about 20 to allow the machine to come to steady state molding conditions. For all



moldings the same injection pressure : 175 bar hydraulic pressure and the same injection speed 60% of max were used.

Examples

All examples were made with fluoroelastomers available from Dyneon.

- 5 The fluoroelastomers were mixed with bisphenol AF crosslinking-agent (available from Aldrich Chemical Co.) and onium accelerator. The fluoroelastomer compositions were mixed with oil, predispersed on a carrier, and other curing and compounding ingredients as indicated in the tables of the examples. Mixing of all the samples used for injection molding were mixed on a water cooled Ø.380×750 mm two roll mill available from Agila™ in Belgium. All other
- 10 mixtures were prepared on a water cooled Ø 150×300 mm two roll mill available from Troester in Germany. Standard mixing procedures know to in the industry were used.

Examples 1 to 6 and comparative example C-1

- Examples 1 to 6 and comparative example C-1 were made starting from fluoroelastomer FC-2174 to the compositions given in table 1. Compositions are presented in parts by weight per
- 15 hundred parts by weight of fluoroelastomer (phr) as is custom in the rubber industry. The properties of the fluoroelastomer compositions are given in tables 2-5.

Table 1 : Composition of fluoroelastomer compositions

Compound	C-1	Ex 1	Ex 2	Ex 3	Ex 4	Ex 5	Ex 6
FC-2174	100	100	100	100	100	100	100
MT N-990	30	30	30	30	30	30	30
Oiled black	-	5	10	20	5	5	5
Ca(OH) ₂	6	6	6	6	6	6	6
MgO	3	3	3	3	3	3	3
Carnauba wax	-	-	-	-	1	-	-
Struktol™ WS-280	-	-	-	-	-	1	-
Armeen™ 18D	-	-	-	-	-	-	1



Table 2 : Rheological properties as measured with a Goettfert Moving Die Rheometer

	C-1	Ex 1	Ex 2	Ex 3	Ex 4	Ex 5	Ex 6
ML (Nm)	0.09	0.11	0.11	0.10	0.11	0.11	0.10
MH (Nm)	1.28	1.37	1.30	1.16	1.48	1.55	1.43
MH-ML Nm)	1.19	1.26	1.19	1.06	1.37	1.44	1.33
Ts2 (min.)	0.8	0.8	0.7	0.6	0.8	0.8	0.9
Tc50 (min.)	1.7	1.7	1.6	1.7	1.6	1.6	1.5
Tc90 (min.)	2.3	2.5	2.3	2.6	2.7	2.6	2.8
VMAX (Nm/min.)	2.08	2.02	1.94	1.48	2.09	2.49	2.43

The results in table 2 indicate that the addition of oil carried on carbon black, did not significantly influence the vulcanisation characteristics as measured by the Moving Die Rheometer.

Example 3 had a significantly higher filler content because of black carrying the oil.

It is this side effect that had a minor influence on some of the MDR values by rendering the compound less flexible.

Table 3 : Mooney scorch test results

	C-1	Ex 1	Ex 2	Ex 3	Ex 4	Ex 5	Ex 6
Mmin (inch.pounds)	34	34	30	11	34	36	28
T3 (min.)	31	>60	>60	>60	38	48	56
T18 (min.)	>60	>60	>60	>60	>60	>60	>60

In all cases, the scorch safety as quantified by T3 increased with the use of oiled carbon black (a more flat curve was noticed). In fact the measured T3 values were for all oil containing samples significantly higher than the comparative, example 3, with the highest oil content, had a significantly lower compound viscosity as given by Mooney scorch minimum.



Table 4 : Vulcanisate physical properties measured on post cured test plates.

	C-1	Ex 1	Ex 2	Ex 3	Ex 4	Ex 5	Ex 6
Hardness Shore A(2")	76	79	80	83	80	80	80
Modulus 100% (MPa)	6.6	7.4	7.6	8.5	7.0	7.6	8.8
Tensile strength a/b (MPa)	15.0	14.1	13.8	11.1	13.5	13.6	13.7
Elongation % at break	195	175	165	130	165	170	145

These data show that the use of oil does not detract significantly on the physical properties of the fluoroelastomer used. The differences in hardness and in elongation seen for example 3 is typical for fluoroelastomers with higher loads of filler as is here also the case.

Table 5 : Results of Goettfert Rheovulkameter test

	C-1	Ex 1	Ex 2	Ex 3	Ex 4	Ex 5	Ex 6
Total volume (mm ³)	1310	1400	2067	7242	1866	1435	3127
Max VOL/s (mm ³ /s)	29.00	31.25	48.63	103.20	72.25	34.25	84.50

The rheovulkameter data of table 5 present a comparison of flow behaviour and the much larger total injected volumes of the oil containing mixtures is evident as well as the significantly higher maximum injected volume speeds. Furthermore using oil in combination with a standard processing aids at 1 phr level shows dramatic differences in flow behaviour depending on the type of standard processing aids suggesting a synergistic effect with low levels of Carnauba Wax or Armeen™ 18D, as can be seen in examples 4, 5 and 6.

Examples 7 to 10 and comparative examples C-2 and C-3

In examples 7 to 10 fluoroelastomer compounds were made, starting from Dyneon E-15948, to which 1.5% active oil carried on Calcium silicate containing 70% wt oil(further called oiled Calciumsilicate 70%) was added, before addition of the other ingredients (indicated as E-15948 1.5% in table 6). Examples 8 and 10 further contain Carnauba wax, a conventional processing aid. The kind and amount of additives uses is given in table 6. Comparative examples C-2 and C-3 were made with E-15948 as is : without added oil. Comparative example C-3 also contains carnauba wax. The performance of the compositions is given in tables 7 to 12.

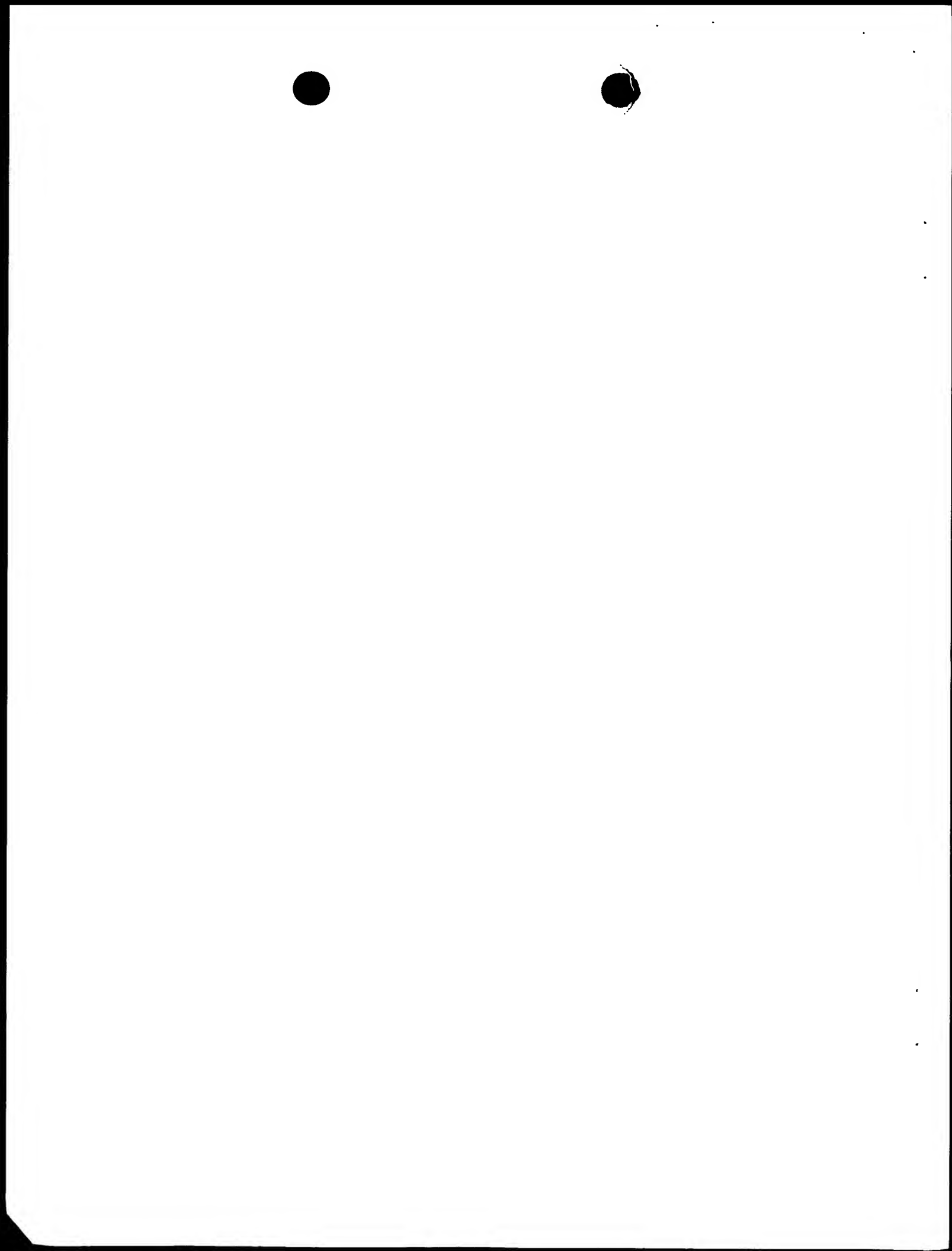


Table 6 : Composition of fluoroelastomer mixtures

Compound	C-2	C-3	Ex 7	Ex 8	Ex 9	Ex 10
E-15948	100	100	-	-	-	50
E-15948 1.5%	-	-	100	100	100	50
MT N-990	30	30	30	30	30	30
Ca(OH) ₂	6	6	6	6	6	6
MgO	3	3	3	3	3	3
Oiled Calciumsilicate 70%	-	-	-	-	3.57	-
Carnauba wax	-	0.5	-	0.5	-	0.5

Table 7 : Vulcanisation behaviour :Results of Goettfert MDR test (test time : 6 min)

	C-2	C-3	Ex 7	Ex 8	Ex 9	Ex 10
ML (Nm)	0.15	0.15	0.16	0.16	0.17	0.15
MH (Nm)	1.29	1.33	1.26	1.34	1.14	1.38
MH-ML (Nm)	1.14	1.18	1.10	1.18	0.97	1.23
Ts2 (min.)	0.7	0.8	0.6	0.7	0.6	0.7
Tc50 (min.)	1.8	1.8	1.6	1.5	1.9	1.6
Tc90 (min.)	2.4	2.5	2.0	2.0	2.6	2.2
VMAX (Nm/min.)	1.89	1.89	2.03	2.18	1.28	2.16

- 5 The data show that no major differences in rheological properties, measured with the Goettfert MDR, were observed.

Table 8 : Results of Mooney scorch test

	C-2	C-3	Ex 7	Ex 8	Ex 9	Ex 10
Mmin (inch.pounds)	47	45	49	47	39	47
T3 (min.)	>60	54	>60	53	>60	41
T18(min.)	>60	>60	>60	>60	>60	>60



The results indicate that compounds containing carnauba wax had a somewhat inferior scorch safety, compared to samples without carnauba wax but with oil.

Table 9 : Vulcanisate properties (press cured 7 min at 177 °C)

	C-2	C-3	Ex 7	Ex 8	Ex 9	Ex 10
Hardness Shore A(2'')	74	74	74	74	70	73
Modulus 100% (MPa)	4.1	3.8	4.0	4.0	3.4	4.0
Tensile (MPa)	9.7	8.1	7.8	7.3	7.5	7.4
Elongation %	280	260	245	250	260	250

- 5 The data show again that the presence of mineral oil in the composition does not substantially alter the mechanical properties.

Table 10 : vulcanisate properties after post cure (16 hrs 230°C)

	C-2	C-3	Ex 7	Ex 8	Ex 9	Ex 10
Hardness Shore A(2'')	77	77	77	78	77	77
Modulus 100% (MPa)	5.2	5.9	6.0	6.6	5.5	6.5
Tensile (MPa)	12.7	13.9	13.8	13.8	13.7	14.2
Elongation %	220	205	205	185	215	190

- 10 After post cure (nearly all applications of fluoroelastomers use post cured articles) differences in properties are even smaller than after press cure.

- 15 The compounds of examples 7 to 10 and comparative examples C-2 and C-3 have been tested for their injection molding processing properties. The test was set up such that data and samples were collected after reaching steady state molding conditions at minimal cycle time (> 20shots after start up with warm machine) and this at 190°C real mold temperature. Further test conditions see above. In a first experiment, O-rings were molded. The results are given in table 11.



Table 11 : Injection molding (O-rings)

	C-2	C-3	Ex 7	Ex 8	Ex 9	Ex 10
Release rating	5	7-8	6-7	8	8	8
Sprue behavior	6-7	8	6-7	8	8	8
Plastization stroke (mm)	6.2	6.2	6.2	6.0	6.1	6.2
Moldfill time (sec)	2.1	2.0	2.2	1.4	1.3	1.8
Heating time (sec)	52	50	45	40	60	45
ID	48.14	48.13	47.81	47.79	47.37	47.92

Comparison of mold fill times as flow quantification shows dramatically shorter fill times if 4 phr oil is present in the composition. Similarly 1.5 phr or 0.75 phr oil combined with 0.5 phr carnauba wax show substantial shorter fill times. Comparing mold fill times of examples C-2, C-3, Ex 7 with Ex8 and 10 makes a synergistic effect between low quantities of Carnauba Wax and oil evident.

When comparing the important processing parameters mold release and sprue behaviour the improvements with the oil and the combinations with the low level of Carnauba Wax are again evidenced. Knit-line were not observed for the examples.

An injection molding test with a spiral mold was done in the same way (see also test conditions described earlier). The results are given in table 12.

Table 12 : Injection molding spiral mold

	C-2	C-3	Ex 7	Ex 8	Ex 9
Plast stroke (mm)	6	6	6.2	6.2	6.4
Flow path length (mm)	229	228	228	235	342
Inj. Piston halt after (sec)	12.4	12.5	12.5	12.6	12.7
time to pass 100mm (sec)	0.97	0.93	1.02	0.55	0.74
time to pass 200mm (sec)	8.89	8.33	8.52	6.67	3.15
Time 100 to 200mm (sec)	7.9	7.4	7.5	6.1	2.4
Heating time (sec)	38	40	28	28	44



The time to pass data indicating flow speeds show again the synergistic effect when combining oil and low levels of Carnauba Wax. Ex-9 shows that oil levels of 4 phr give a dramatic effect on flow speed and ultimate flow length.

5 Example 10bis, 11, 12 and comparative examples C-4 to C-6

Examples 10bis, 11 and 12 were made with various fluoroelastomer polymer compounds (differing in monomer types and ratio's), available from Dyneon, as given in table 13. To all compounds were added 30 phr Huber N 990 MT, 6 phr calcium hydroxide and 3 phr magnesium oxide. The compounds further contained oil added as oiled black (50% oil) as given in table 13.

10 Comparative examples C-4, C-5 and C-6 were made without added oiled black.

Table 13 : composition of fluoroelastomer compounds

Compound	Ex 10b	C-4	C-5	Ex 11	C-6	Ex 12
Dyneon™ FE-5840Q	100	100	-	-	-	-
E-14251A	-	-	100	100	-	-
BRE-7132X	-	-	-	-	100	100
Oiled Black (50%)	8	-	-	8	-	8

A vulcanisation characterisation test was done using the Goettfert MDR test (6 min at 180°C ; 12 min at 170°C and 120 min at 140°C). The use of oiled carbon black did not influence the vulcanisation behaviour as measured in this way. Also the physical properties were not different with or without oil.

However, a clear difference was observed when the flow behaviour was measured using a Goettfert rheovulkameter with spiral mold. The results are given in table 14.

Table 14 : Goettfert rheovulkameter (spiral mold)

	Ex 10b	C-4	C-5	Ex 11	C-6	Ex 12
Total volume (mm ³)	2099	1398	1948	2060	1175	1592
Max VOL/s (mm ³ /s)	49.50	25.50	32.93	58.08	23.25	39.75



In all cases an increase in volume and speed was noticed for the samples containing oil compared to the same samples without oil added, thus showing that the effects reported above are also evident in other types of fluoroelastomer polymers .

5 Examples 13 to 18

In examples 13 to 18, compounds were made with fluoroelastomer FC-2176. To all samples were added 30 phr Huber N 990 MT, 6 phr calciumhydroxide and 3 phr magnesiumoxide. Additionally Multiblack or oiled CaSilicate (with 70% oil) were added. The composition of the examples is given in table 15.

10

Table 15 : Composition of fluoroelastomer compounds

COMPOUND	Ex 13	Ex 14	Ex 15	Ex 16	Ex 17	Ex 18
Oiled black(50%)	1	2	3	5	-	-
Oiled	-	-	-	-	1.43	2.86
CaSilicate(70%)						

A vulcanisation behavior test was done using the Goettfert MDR test (6 min at 180°C). The use of oil did not influence the vulcanisation behaviour as measured in this way, even not at the higher level of added oil (example 16). Also the physical properties were not different when different amounts of oil were added.

A high scorch safety, as measured by the Scorch Mooney test was noticed (all values T3 and T18 >60).

20 The flow behaviour was measured with a Goettfert rheovulkameter with spiral mold. The results are given in table 16.

Table 16 : Flow behaviour, measured with Goettfert rheovulkameter

	Ex 13	Ex 14	Ex 15	Ex 16	Ex 17	Ex 18
Total volume (mm ³)	1323	1344	1370	1442	1467	1507
Max VOL/s (mm ³ /s)	28.75	28.50	31.50	34.75	33.91	33.25



A steady increase in total volume and speed was noticed as the concentration of oil increased. A small increase in compression set values was noticed as the amount of oil increased. The results are given in table 17.

5 Table 17 : Compression set resistance (Method B : 25% deformation)

	Ex 13	Ex 14	Ex 15	Ex 16	Ex 17	Ex 18
% SET 70 HRS @ 200°C	21	21	22	24	22	23
% SET 168HRS @200°C	30	31	32	37	33	35

Examples 19 to 21 and comparative example C-6

In examples 19 to 21, compounds were made with fluoroelastomer FC-2181. To all samples were added 30 phr Huber N 990 MT, 6 phr calciumhydroxide and 3 phr magnesiumoxide.

- 10 Additionally oiled black and carnauba wax were added as given in table 18. Comparative example C-6 was made in the same way, but without the addition of oil.

Table 18 : Composition of fluoroelastomers

Compound	C-6	Ex 19	Ex 20	Ex 21
oiled black (50%)	-	3	10	7.5
Carnauba wax	0.75	0.50	0.50	0.25

- 15 Rheological and physical behaviour was tested for example 19 and comparative example C-6. No difference could be seen in the Goettfert MDR test or in physical behaviour. However, a clear difference could be seen when the flow behaviour was measured using a Goettfert rheovulkameter with spiral mold. The results are given in table 19.

20 Table 19 : Flow behaviour as measured with a Goettfert rheovulkameter (spiral mold)

	C-6	Ex 19	Ex 20	Ex 21
Total volume (mm ³)	1246	1311	2447	1890
Max VOL/s (mm ³ /s)	35.41	42.91	95.25	79.38

The volume and speed increased when higher amount of oil were added. Very high values were obtained when 5phr oil were used together with 0.5 phr carnauba wax. Samples made with 0.25



phr carnauba Wax and 3.75 phr oil (example 21) showed much better flow properties compared to a reference that contained 0.75 phr carnauba wax and no oil (C-6). This further illustrates the synergistic effect on improved flow behaviour of a fluoroelastomer compound containing a mixture of a conventional processing aid, such as Carnauba wax and mineral oil.

5

Examples 22 to 27 and comparative example C-7

In examples 22 to 27, compounds were made with fluoroelastomer FC-2174. To all samples were added 30 phr Huber N 990 MT, 6 phr calciumhydroxide and 3 phr magnesiumoxide. Additionally various oils (different in composition), as given in table 20 were added.

- 10 Comparative example C-7 was made without the addition of oil. The properties of the fluoroelastomer compositions are given in tables 21 to 24.

Table 20 : Composition of fluoroelastomer compounds

Compound	C-7	Ex 22	Ex 23	Ex 24	Ex 25	Ex 26	Ex 27
PennzUltra™ 1122	-	4	-	-	-	-	-
PennzUltra™ 1199	-	-	4	-	-	-	-
PennzNap™ 60	-	-	-	4	-	-	-
PennzNap™ 500	-	-	-	-	4	-	-
PennzNap™ 1500	-	-	-	-	-	4	-
Saltex™	-	-	-	-	-	-	4

- 15 Table 21 : Results of Goettfert MDR test

	C-7	Ex 22	Ex 23	Ex 24	Ex 25	Ex 26	Ex 27
ML (Nm)	0.12	0.10	0.10	0.09	0.10	0.10	0.10
MH (Nm)	1.41	1.30	1.28	1.28	1.28	1.29	1.31
MH-ML (Nm)	1.29	1.20	1.18	1.19	1.18	1.19	1.21
Ts2 (min.)	0.8	0.8	0.8	0.9	0.8	0.8	0.8
Tc50 (min.)	1.8	1.8	1.8	1.8	1.8	1.8	1.7
Tc90 (min.)	2.5	2.8	2.7	2.8	2.8	2.8	2.7
VMAX (Nm/min.)	2.04	1.79	1.79	1.85	1.76	1.67	1.75



The table indicates that almost no differences occur in the MDR test, using different oils, and compared to a reference, without oil added.

Table 22 : Mooney scorch, at 121 °C

	C-7	Ex 22	Ex 23	Ex 24	Ex 25	Ex 26	Ex 27
Mmin (inch.pounds)	37	29	29	28	29	30	30
T3 (min.)	54	>60	>60	>60	50	49	48
T18 (min.)	>60	>60	>60	>60	>60	>60	>60
T18-T3 (min.)		0	0	0			

5

Scorch safety given by T3 is equivalent or better for the oil containing mixtures when compared to comparative example C-7.

Table 23 : vulcanisate properties after post curing

	C-7	Ex 22	Ex 23	Ex 24	Ex 25	Ex 26	Ex 27
Hardness Shore A(2")	76	74	74	77	77	75	77
Modulus 100% (MPa)	5.7	5.3	5.3	5.5	5.2	4.6	5.2
Tensile (Mpa)	11.5	11.4	10.2	11.4	9.9	9.6	9.1
Elongation %	180	190	175	180	170	180	175

10

The data show that none of the different oils tested has a substantial effect on the mechanical properties of the vulcanisate.

Table 24 : Goettfert rheovulkameter results (spiral mold)

	C-7	Ex 22	Ex 23	Ex 24	Ex 25	Ex 26	Ex 27
TOTAL VOLUME (mm3)	1135	2195	2106	2175	2095	1977	1822
MAX VOL/s (mm3/s)	21.25	46.87	47.16	50.08	46.75	44.83	46.25

15

Flow data of table 24 show that all oils provide dramatic improvement of flow behaviour. Some differences between the oils exist however all oils irrespective of their composition



provide a dramatic improvement in flow speed and ultimate flow path length as given by total volume.



CLAIMS

1. Use of a mineral oil in a fluoroelastomer composition comprising a fluoroelastomer to improve the flow of said composition during processing to form an article therefrom and/or
5 to improve the release from a mold of a vulcanized article produced from said fluoroelastomer composition.
2. Use according to claim 1 wherein said mineral oil is present in said fluoroelastomer composition in an amount of 0.25 to 15 parts by weight for 100 parts by weight of
10 fluoroelastomer.
3. Use according to claim 1 wherein said mineral oil is at least partially adsorbed on a carrier.
4. Use according to claim 3 wherein said carrier comprises particles capable of adsorbing said
15 mineral oil.
5. Use according to claim 4 wherein said particles are selected from the group consisting of carbon black and inorganic particles.
6. Use according to any of the previous claims wherein said fluoroelastomer composition
20 further comprises a wax.
7. Use according to claim 6 wherein said wax is a vegetable wax and is contained in said fluoroelastomer composition in an amount of less than 2 parts by weight per 100 parts by
25 weight of fluoroelastomer.
8. Method of making a fluoroelastomer article comprising the steps of providing a fluoroelastomer composition comprising a fluoroelastomer and a mineral oil and processing said composition to form said fluoroelastomer article by means of a processing technique
30 selected from the group consisting of extrusion, injection molding, transfer molding, compression molding and combinations thereof.



9. Method according to claim 8 wherein said mineral oil is present in said fluoroelastomer composition in an amount of 0.25 to 15 parts by weight for 100 parts by weight of fluoroelastomer.
- 5 10. Method according to claim 8 wherein said mineral oil is at least partially adsorbed on a carrier.
11. Method according to claim 10 wherein said carrier comprises particles capable of adsorbing said mineral oil.
- 10 12. Method according to claim 11 wherein said particles are selected from the group consisting of carbon black and inorganic particles.
13. Method according to any of claims 8 to 12 wherein said fluoroelastomer composition further
- 15 comprises a wax.
14. Method according to claim 13 wherein said wax is a vegetable wax and is contained in said fluoroelastomer composition in an amount of less than 2 parts by weight per 100 parts by weight of fluoroelastomer.
- 20 15. Method according to any of claims 8 to 14 wherein said fluoroelastomer composition comprises a vulcanization system and wherein said method includes the step of vulcanization.
- 25 16. Fluoroelastomer composition comprising a fluoroelastomer and a mineral oil, said composition being free of vegetable wax or containing vegetable wax in an amount of less than 2 parts by weight per 100 parts by weight of fluoroelastomer.
- 30 17. Fluoroelastomer composition according to claim 16 wherein said fluoroelastomer composition is free of any wax or contains a total amount of vegetable and non-vegetable wax of less than 2 parts by weight per 100 parts by weight of fluoroelastomer.



18. Fluoroelastomer composition according to any of claims 16 or 17 wherein at least part of said mineral oil is adsorbed on a carrier.
- 5 19. Fluoroelastomer composition according to claim 18 wherein said carrier comprises particles capable of adsorbing said mineral oil.
20. Fluoroelastomer composition according to claim 19 wherein said particles are selected from the group consisting of carbon black and inorganic particles.
- 10 21. Fluoroelastomer composition according to any of claims 16 to 20 wherein said mineral oil is comprised in the fluoroelastomer composition in an amount of 0.25 to 15 parts by weight for 100 parts by weight of fluoroelastomer.
- 15 22. Fluoroelastomer composition according to any of claims 16 to 21 further comprising a vulcanization system.
- 20 23. Method of making a fluoroelastomer composition having improved flow characteristics when processed, said method comprising the steps of blending together a mineral oil and a fluoroelastomer to obtain a fluoroelastomer composition that is free of vegetable wax or alternatively to blend together a mineral oil, a fluoroelastomer and a vegetable wax to obtain a fluoroelastomer composition that contains a vegetable wax in an amount of less than 2 parts by weight for 100 parts by weight of fluoroelastomer.
- 25 24. Method according to claim 23 wherein said mineral oil is adsorbed on a carrier when blended with said fluoroelastomer.
- 25 25. Method according to claim 24 wherein said carrier comprises particles capable of adsorbing said mineral oil.
- 30 26. Method according to claim 25 wherein said particles are selected from the group consisting of carbon black and inorganic particles.



INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/18502

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C08L27/12 C08K9/08 //(C08L27/12,91:00)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 948 830 A (MARTIN JON W ET AL) 14 August 1990 (1990-08-14) column 3; claims; table ---	1-26
A	WO 96 00761 A (DU PONT ;IER IND INC (US)) 11 January 1996 (1996-01-11) page 10, line 13-15; examples ---	1-26
A	US 3 929 707 A (BERG GERHARD ET AL) 30 December 1975 (1975-12-30) claims -----	1-26

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4948830	A	14-08-1990	NONE	
WO 9600761	A	11-01-1996	US 5459202 A WO 9600761 A1	17-10-1995 11-01-1996
US 3929707	A	30-12-1975	DE 2332796 A1 AU 7054274 A BE 816976 A1 CA 1057878 A1 DD 111912 A5 FR 2235153 A1 GB 1464279 A IT 1016183 B JP 50043144 A JP 54004380 B NL 7406341 A SU 509244 A3	16-01-1975 08-01-1976 16-10-1974 03-07-1979 12-03-1975 24-01-1975 09-02-1977 30-05-1977 18-04-1975 06-03-1979 31-12-1974 30-03-1976



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(54) Title: ELASTOMER SEAL			
(57) Abstract			
<p>Seals capable of containing corrosive liquid and/or vapor of, e.g., HCFCs, are made of cured blends of (a) CTFE/VF₂ elastomer, (b) chlorine-free fluoroelastomer, and (c) 1 to 20 wt.% of hydrocarbon polymer, based on the combined weight of (a) and (b). The blends are homogeneous and coherent wherein the hydrocarbon polymer is not visible at 165X magnification as a separate phase within the matrix of the blend of (a) and (b), and the blend is free of internal cracks and voids.</p>			

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TITLE**ELASTOMER SEAL****BACKGROUND OF THE INVENTION**

5 The present invention relates to fluoroelastomer seals and compositions therefore, for sealing such fluids as fluorocarbons, chlorocarbons, hydrogen fluoride and hydrogen chloride, and mixtures thereof.

10 An important use of elastomers is for the production of seals, such as gaskets and O-rings for sealing fluids. Elastomers generally are able to act as a seal because of their resilience and general impermeability to many fluids. This is important not only to avoid the loss or contamination of valuable materials, but also to protect personal safety, health and the environment.

15 The requirements for a suitable seal are many. First, of course, it must not degrade or lose its elasticity in contact with the fluids being handled, even at extremes of temperature and pressure. It must not allow these fluids to pass through them easily by permeation. It must not react with these fluids or contaminate them with impurities. And the material must not swell appreciably in contact with the fluids being handled, even at elevated temperatures. For example, if an O-ring in contact with a moving surface swells appreciably, it may be extruded into a close-clearance area where it will be torn by friction.

20 When an O-ring swells while in contact with a fluid under pressure or high temperature, and the pressure or temperature is then reduced, the O-ring may shrink from its extruded position in a way that causes fluid leakage to occur.

25 Fluoroelastomeric polymers have been utilized extensively for such sealing applications because of their outstanding chemical inertness, solvent resistance and their resistance to high temperatures. In such applications their higher cost than other elastomers is readily justified by their longer life and superior performance.

30 However, existing fluoroelastomers are not by themselves suitable for sealing certain organic fluorochemical fluids under typical conditions. Because of the chemical similarity of fluorochemical fluids to fluoroelastomers, the fluids tend to dissolve in the fluoroelastomers and thereby cause its swelling and physical deterioration. When such fluorochemicals are manufactured, many of the process streams also contain chlorocarbons and highly corrosive hydrofluoric acid (HF) or hydrochloric acid (HCl), adding to the severity of

35 attack. In particular, 2,2-dichloro-1,1,1-trifluoroethane (HCFC-123) is very aggressive in surface attack on seals. HCFC-123 has therefore proven to be one of the most difficult products for which to find a satisfactory seal.

There is a need in the fluorochemical industry for a fluorine-containing elastomeric seal especially suitable for sealing, including containing fluorocarbons, chlorocarbons, hydrogen fluoride, hydrogen chloride and the like, and mixtures thereof.

5

SUMMARY OF THE INVENTION

The present invention satisfies this need by providing a seal comprising cured, coherent, homogeneous elastomer blend comprising (a) chlorotrifluoroethylene/vinylidene fluoride (CTFE/VF₂) elastomer, (b) chlorine-free fluoroelastomer, and (c) a minor proportion with respect to the combined weight of (a) and (b) of hydrocarbon polymer.

10

Surprisingly, the hydrocarbon polymer, although present in a minor amount; e.g., 1 to 20 wt%, based on the weight of components (a) plus (b) in the blend, and although incompatible with the fluoroelastomers, nevertheless imparts a significant reduction in fluorochemical permeability of the seal.

15

The present invention also provides the curable, coherent homogeneous composition blend useful for fabrication into the seal and curing. The composition is prepared by compounding components (a), (b), and (c) together with curing agent at elevated temperature; e.g., at least 60°C, but below the curing temperature for the blend.

20

Surprisingly, the hydrocarbon polymer disappears into the resultant composition; i.e., it is not visible as a separate phase in the elastomer matrix under 165 x magnification, whereby the composition is homogeneous in character. In addition, neither cracks nor voids, which would be expected from the presence of component (c) in the incompatible matrix of components (a) and (b), are visible under this magnification, giving the composition its coherent character.

25

The seals of this invention are effective in handling the more aggressive fluorochemicals used for refrigeration such as 2,2-dichloro-1,1,1-trifluoro-ethane (HFC-123) and substitutes for CFCs together with other fluorocarbons, chlorocarbons, HF, HCl or mixtures thereof.

30

DETAILED DESCRIPTION OF THE INVENTION

The CTFE/VF₂ polymer used to make composition of the present invention, which, in turn, is used to make the seals of the present invention generally contains about 25-50 mol% chlorotrifluoroethylene, the balance being vinylidene fluoride, and is curable to an elastomer. This product is commercially available through 3M as Kel-F® elastomer. The term "elastomer" as used herein means a polymer which exhibits little plastic flow and quick or nearly complete recovery from an extending force. The extending force can

35

stretch the polymer to 100% without breaking. After such stretch and being held for 5 minutes and then released, it will retract to within 10% of its original length within 5 minutes after release.

Chlorine-free fluoroelastomer (component b) includes both
5 perfluoroelastomer and hydrogen-containing fluoroelastomer. Examples of chlorine-free fluoroelastomer include tetrafluoroethylene/perfluoro(alkyl vinyl) ether (TFE/PAVE) polymer and vinylidene fluoride/hexafluoropropylene (VF₂/HFP) polymer, curable to elastomer.

With respect to the TFE/PAVE polymer, this polymer contains
10 sufficient PAVE to provide elastomer properties when cured. PAVE includes perfluoro(alkoxy alkyl vinyl)ether (PAAVE). The alkyl group of the PAVE preferably contains 1 to 8 carbon atoms. Preferably the PAVE is perfluoro(methyl vinyl)ether (PMVE) or PAAVE. TFE/PMVE elastomer is available from DuPont and TFE/PAAVE polymer is available from Daikin as
15 Dai-el Perfluor GA-55® fluoroelastomer. The amount of PAVE will generally be about 25 to about 40 mol% PAVE and complementally to total 100 mol% about 75 to about 60 mol% TFE. When less than about 25% of the PAVE is added, the copolymer generally does not exhibit sufficiently elastomeric properties; addition of more than about 40% of the PAVE is difficult.

20 A wide variety of hydrogen-containing fluoroelastomers can be used in this invention. They are copolymers of at least one fluorinated monomer, but may incorporate monomers containing no fluorine. These polymers commonly, but not universally, incorporate vinylidene fluoride (VF₂) as a monomer. The most common fluoroelastomers are copolymers of VF₂ with
25 hexafluoropropylene (HFP) and optionally tetrafluoroethylene (TFE). However, the use of other fluoromonomers and of monomers that do not contain fluorine is well known. Other monomers than can be used include hydrocarbon olefins such as ethylene (E) or propylene (P), and PAVE, as described above. A preferred PAVE is perfluoro(methyl vinyl)ether (PMVE). Fluoroelastomers
30 incorporating such monomers include TFE/VF₂/PMVE, E/TFE/PMVE, and TFE/P copolymers.

The VF₂/HFP polymer is a preferred member of the class of hydrogen-containing fluoroelastomers. The copolymers generally contain from 70% to 30% by weight of vinylidene fluoride units and from 30% to 70% by
35 weight of hexafluoropropylene (HFP) units. When the fluoropolymer contains less than 30% of HFP units it tends to become non-elastic. Production of a fluoropolymer containing more than 70% HFP is difficult. This polymer is available, for example, as Viton® fluoroelastomer by DuPont.

To provide or enhance curability, fluoroelastomers may include reactive cure site moieties derived from small concentrations of cure site monomers in addition to the primary monomers described above. Such monomers can include, for example, bromine-containing fluoroolefins and fluoro(vinyl ethers), and cyano-substituted fluoro(vinyl ethers). Cure site monomers may be present in concentrations up to about 3 mol%. Alternatively or additionally, chain transfer agents that are not perfluorinated can be used in the polymerization reaction to introduce desirable fragments into the polymer for curing purposes. Such agents include iodinated compounds that result in bound iodine in the polymer, commonly at one or both ends of the molecule. When iodinated compounds are used in polymerization, the resulting concentration of iodine in the fluoroelastomer is at least 0.001 wt%, desirably at least about 0.05 wt%, and preferably at least about 0.1 wt%. The hydrogen-containing fluoroelastomer is generally amine or polyol curable.

The CTFE/VF₂, and chlorine-free fluoropolymers curable to fluoroelastomers, such as the TFE/PAVE and VF₂/HFP polymers described above are typically individually supplied with curing agents and compounding ingredients, such as triallylisocyanurate and/or organic peroxide (curing agents), compounding oil, and reinforcing agent such as carbon black, in amounts ranging from 1-5 wt% (curing agent), 1-5 wt% (compounding oil), and 5-30 wt% (carbon black) based on the total weight of the entire individual polymer composition. Each polymer is in a compoundable form; e.g., gum, so that they may be blended together. Each polymer might have different or the same curing agents and compounding ingredients as compared to the other polymer.

It is important that the compounding ingredients used in the blends of this invention should be free of any ingredient which is reactive with fluorochemical under expected conditions of use; e.g., metal oxides or carbonates such as CaO, PbO, CaCO₃, should not be present if these blends are to be used in contact with HF or HCl.

The hydrocarbon polymer used in the invention (component (c)) generally has sufficient flow at the usual compounding temperature of 60°C-120°C so as to be able to be homogenized into the matrix blend of components (a) and (b). In the case of crystalline hydrocarbon polymers, this is accomplished by relatively low molecular weight for the polymer, e.g., 1,000 to 10,000. In the case of amorphous (elastomeric) hydrocarbon polymers, this is achieved by the polymer having a glass transition temperature (T_g) less than 60°C. Representative hydrocarbon polymers include ethylene and propylene

polymers, such as polyethylene, polypropylene, ethylene/propylene rubbers with or without a third monomer such as a nonconjugated diene (EPDM).

Proportions of components (a) and (b) can vary widely, e.g., 10 to 90 wt% of (a) and complementally to total 100 wt%, 90 to 10 wt% of (b). Both are fluoropolymers and can be readily blended together. Preferably, the proportion of the CTFE/VF₂ polymer will be from about 10 to 50 wt% of the total amount of (a) plus (b). For ease of compression molding, however, it is preferred that the proportion of CTFE/VF₂ polymer be no greater than 20 wt%. When less than 10 wt% of the CTFE/VF₂ polymer is present, the thermal resistance becomes less than desired. Component (b) can be either a single chlorine-free curable polymer or a mixture thereof, such as a mixture of TFE/PAVE polymers, VF₂/HFP polymers or a mixture of both. These weight percents refer to the fluoropolymers but also generally apply to the individual fluoropolymer compositions which contain their respective curing agents and compounding ingredients, which will be in similar proportion with respect to their associated fluoropolymer. Gums which are curable to elastomer are typically made available with curing and compounding ingredients in amounts not disclosed by the supplier and not determinable by analysis, but it is believed that the individual polymer (gum) composition will usually be at least 80 wt% polymer.

The proportion of hydrocarbon polymer will depend on the particular hydrocarbon polymer used and its compoundability at particular concentrations, in terms of achieving coherence and homogeneity of the ultimate blend. This polymer is used in an amount which is a minor amount relative to (a) plus (b) and which is effective to decrease the permeability of the seal to the fluorochemical. Typically this can be achieved by 1 to 15 wt% of the polymer based on the weight of components (a) plus (b), and preferably from about 2 to 10 wt% of the hydrocarbon polymer.

In formulating the curable, coherent, homogeneous compositions of this invention, it is important that the various components be thoroughly mixed. Methods of adding and blending curing agents and compounding ingredients into a polymer are well known in the art. It is usually done on a roll mill in which the first polymer component is placed on a heated pair of rolls to form a band around the roll drum and the other components are added stepwise. Blending is done by cutting the polymer band with a knife and adding the cut portion back to the roll in a different location, a process called crosscutting. Examination of cross sections of compositions of the present invention after compounding and after fabrication into articles such as O-rings and curing, under 165 x magnification surprisingly have shown both the compositions and

cured blends to be coherent and homogenous. Other mixing and blending apparatus suitable for carrying out this process include a Banbury mixer, a mixing extruder, or other devices can be used. After compounding to form the composition, the composition can be placed in a mold under pressure to form
5 the desired shape of the seal, wherein the composition is then heated to cure the composition to obtain the seal as a result thereof. Often this curing is carried out in two steps; first, initial curing within the mold followed by postcure outside of the mold.

The ability of the seal to withstand fluorochemical is generally based
10 on testing of exposure to hydrogen fluoride at elevated temperature and elevated pressure, depending on the test. An HCFC, such as HCFC-123 may also be present. The tests include chemical resistance as evidenced by volume swell and weight gain of the seal. Retention of the elastomeric character of the seal can be judged by the testing for change in hardness. In the latter case, if the seal
15 either increases or decreases in hardness, the seal can fail by virtue of the seal becoming brittle or too soft (respectively).

Testing of Existing Elastomers on Exposure to HCFC-123

As a first step in seeking a suitable seal for fluorochemical such as
20 HCFC-123, existing elastomers were subjected to a mild exposure test, by immersion of the commercially available elastomer in HCFC-123 for seven days at 54°C. Even in this mild exposure test, none of these elastomers were suitable.

In greater detail, each elastomer (compounded and cured) in sheet form was cut into strips 3 x 0.6 x 0.3 cm and each strip was immersed in a
25 horizontally disposed closed 12 ml vial (1.6 cm I.D. x 7.6 cm long) containing 5 ml of the HCFC-123 under the time and temperature conditions mentioned above. Volume swell of each elastomer strip was determined at the end of the seven days' exposure while still immersed in the HCFC-123, by measuring the increase in length of the strip and cubing the resultant ratio of increased length
30 to original length, assuming the swell was uniform in each dimension. The weight gain was measured one hour after the strip was removed from the HCFC-123. The test results are shown in the following Table A.

Table A

Elastomer	% Vol. Swell	% Wt. Gain
Nordel® ethylene-propylene	-12%	-13%
Viton® A fluoroelastomer	63%	44%
Adiprene® L polyurethane	319%	164%
Thiokol® FA polysulfide	7%	4%
Silicone rubber	142%	35%
Buna S styrene butadiene	21%	24%
Polyisoprene natural rubber	143%	28%
Hypalon® chlorosulf. polyethylene	45%	11%
Neoprene® W polychloroprene	37%	27%
Isobutylene isoprene butyl rubber	39%	15%
Buna N acrylonitrile butadiene	61%	59%

5 All the above elastomers were considered unsatisfactory under this mild exposure to HCFC-123 because of excessive volume swell and weight gain. The only sample with a reasonably low swell and weight gain under these moderate temperature conditions was the polysulfide, but it was ruled out because of its known poor resistance to acids and poor mechanical properties including compression set.

10 A second set of immersion tests were carried out on 19 various elastomers in strip form as above in boiling HCFC-123 (30°C) for a period of only 8 hours. Results were as follows:

Table B

Elastomer	% Vol. Swell
Styrene-butadiene rubber	16%
Butyl rubber	33%
Nordel® hydrocarbon rubber	-5%
Adiprene® urethane rubber	238%
NBR nitrile	64%
Hypalon® synthetic rubber	44%
Neoprene polychloroprene	16%
Hydrin® polyepichlorhydrin	33%
Alcryn® hydrocarbon TPE	64%
Hytrel® polyester elastomer	69%
Silicone rubber	110%
Thiokol® FA polysulfide	16%
Thiokol® ST polysulfide	77%
Vamac® ethylene acrylic elastomer	186%
Aflas® TFE/propylene copolymer	120%
Viton® A fluoroelastomer	60%
Viton® B fluoroelastomer	82%
Viton® GF fluoroelastomer	77%
Kalrez® fluoroelastomer	56%

The degree of swell (or shrinkage) in only 8 hours at a relatively low temperature would rule out all these materials for extended use.

- 5 A series of tests were run on O-rings of different elastomers exposed to a gaseous mixture of HCFC-123 and AHF (anhydrous HF) at 120°C for 168 hours to simulate the exposure encountered in the use of O-rings as seals in chemical process equipment. Further details of this exposure test are given in the general procedure in the Examples. These conditions of exposure (exposure
- 10 to gaseous chemical mixture for 120°C for 168 hours) in accordance with the general procedure is the Chemical Process Simulation Exposure Test. Seals of the present invention preferably have volume swell of less than 15%, weight gain of less than 15% and change in hardness of less than 15% when exposed to this test, and more preferably less than 10% for each of these parameters. Even
- 15 more preferably, the % volume swell and weight gain is less than 5% for each parameter. CTFE/VF₂ elastomer Kel-F® 3700 was included in this test despite its known limitations on physical properties. TFE/PAAVE polymer (Dai-el

Perfluoro GA-55[®], (hereinafter called GA-55) was also included in this test, along with TFE/PMVE polymer (Kalrez[®] fluoroelastomer 4079 O-rings), with the results shown in Table C.

5

Table C

Fluoroelastomer	% Vol. Swell	% Wt. Gain	Hardness (DA)		
			Start	End	Change
Kel F [®] 3700	24.4	12.5	74	68	-6
GA-55	15.1	2.0	81	77	-4
Kalrez [®] 4079	39.1	28.5	78	70	-8

The GA-55 had a low weight gain, and was relatively good in volume swell and compression set, but not to the desired level. The sample was observed to have some surface blisters, but it was elastic and did not crack when stretched. Two more samples of the GA-55 were made and tested, and all showed the same surface defects. The Kel F[®] proved to be superior in compression set to the other commercial fluoroelastomers tested, but poor in volume swell. Attempts were made to improve the performance of these three products by reformulating their compounding mix, but little or no improvement was shown.

Thus, fluoroelastomers existing prior to the present invention did not provide seals with adequate sealing capacity and chemical resistance and physical integrity to be economically useful for containing such corrosive materials as HCFCs and HF. Normally, materials that will withstand these materials will also withstand chlorocarbons, CFC's and HCl and hydrocarbons as well and be useful as a seal therefor. Curable blends of the present invention are also useful for other applications such as hose.

EXAMPLES

The following examples are illustrative of the invention, wherein parts are by weight unless otherwise indicated.

General Procedure

The compounding ingredients that were used were carbon black to impart compression resistance to the composite, halocarbon oil to impart dynamic properties, swell control and temperature resistance, Diak[®] No. 7 (triallylisocyanurate curing agent) as a secondary curing agent, with Luperco[®] 101XL (organic peroxide curing agent) as the primary peroxide curing agent.

The CTFE/VF₂ polymer was banded on a hot mill at 77°C to 88°C roll temperature for approximately 4 minutes. The carbon black was then

blended into the polymer until incorporated, taking about 7 minutes. The hydrocarbon polymer (polyethylene) was then added, and the mix blended and crosscut until uniform, taking about 3 minutes. Then the Luperco® was added until fully dispersed in the batch, taking another 3 minutes. The halocarbon oil
5 was then added slowly until fully incorporated in the batch, taking about 4 minutes. Finally the Diak® was added, and both sides of the batch were crosscut about seven times to insure uniformity. Then the batch was rolled 5 to 6 times. The time required for Diak® addition and rolling was about 6 minutes. The rubber was then removed from the roll and allowed to cool. The batch
10 temperature when stripped off the roll was about 99°C to 104°C; the mill roll temperature was estimated at 113°C to 118°C. The total mixing time of this first mix (Compound A) was about 25 to 30 minutes.

The second mix was designated as "Compound B," and contained 100 pts of tetrafluoroethylene-perfluoro(methylvinyl) ether copolymer, GA-55,
15 a precompounded gum containing carbon black, oil, and curing agent.

The final blend was composed of various weighed proportions of Compound A and Compound B as will be described in these Examples. Compound B was first pre-blended on the rolls for about 5 minutes to break down the compound and to build the desired mill-roll temperature to about 77°C
20 to 88°C. Then Compound A was added slowly to Compound B on the mill, adding about one-third of the batch each time and crosscutting the blend 2 to 3 times after each addition. After the addition of Compound A was complete, the blend was mixed thoroughly on the mill and crosscut from time to time until the blend was smooth and well blended in appearance. When an adequate mix was
25 accomplished, the blend was rolled on the mill rolls for at least 7 times, and then stripped off the rolls and allowed to cool to room temperature. It was found desirable to let the blend "relax" for at least 12 hours prior to molding to improve the appearance and properties of the finished products.

After rheological testing of the blend to ensure it met desired initial
30 properties, i.e., further compounding was not necessary, it was placed back on the mill for preheating about 4 to 5 minutes, and then stripped off the roll and cut into long strips for feeding to the extruder for preforming into rope. The extruder temperature was about 52°C, with the die temperature about 82°C. A sample of the extruded compound was then examined in the laboratory to make
35 sure it met all required standards. Then O-rings were molded using a 5-minute cure time and 182°C mold temperature. The O-rings were then oven cured for 16 hours at 150°C. Oven curing resulted in optimum physical properties, a

tighter cure and for the liberation of hydrogen fluoride gas and peroxide radicals from the product.

After this preparation of O-rings, the following tests were run:

Physical properties were measured using Monsanto Tensometer T.10 to confirm
5 that the tensile strength, elongation and modulus were comparable to that which
is desired for O-rings, to qualify the O-rings for the more vigorous chemical
exposure tests. The Shore "A" hardness was measured using ASTM Method
D-2240. Cross sections of the O-rings were cut and viewed under 165X
10 magnification to reveal homogeneity and absence of voids or cracks in the
blends making up the O-rings.

Chemical resistance was determined as follows: Two samples of
each composition of size 214 O-ring were tested by exposure to HCFC-123 for
70 hours at 150°C as described below.

After the initial weight was taken on the latter two O-rings in both air
15 and water, the five specimens were suspended on a hang wire in a tightly closed
bomb. One-sixth of the bomb volume was filled with HCFC-123, making sure
that the O-rings were not immersed, and the bomb was placed in the oven at
150°C. Since the HCFC-123 will be converted to gas when the bomb is heated
20 to the oven temperature, this procedure ensured that the O-rings were exposed
only to the gas phase, not the liquid phase. After the 70-hour exposure test, the
bomb was removed from the oven and allowed to cool for one hour at room
temperature. The previously weighed samples were then reweighed, taking
special care to be fast and accurate since the HCFC-123 will volatilize from the
O-ring in a short period of time. The volume change and weight change were
25 measured using ASTM Method D-471.

Example 1

The following blends were made and fabricated into O-rings
following substantially the general procedure as described above.

Ingredient	Composition - Wt. %					
	1	2	3	4	5	6
TFE/PAVE GA-55	75.00	75.00	75.00	75.00	50.00	25.00
CTFE/VF2 (Kel F® 3700)	15.92	14.97	14.13	13.37	27.03	42.86
EPDM (Vistalon® 404)	-	-	-	-	6.76	4.76
Polyethylene (AC-Poly 617A)	1.59	2.99	4.24	5.35	-	-
N-990 Carbon Black	6.37	5.99	5.65	5.34	13.51	23.81
Halocarbon Oil	0.48	0.45	0.42	0.40	1.01	1.43
Diak® #7	0.32	0.30	0.28	0.27	0.68	0.95
Luperco® 101XL	0.32	0.30	0.28	0.27	1.01	1.19

Test results for these compositions are given in succeeding Examples.

Example 2

- Compositions 1 and 2 were fabricated into O-rings following substantially the same general procedure as described in the general procedure, and they were then exposed to a gaseous mixture of chlorodifluoroethane (HCFC-22) refrigerant and anhydrous hydrofluoric acid (AHF) at 50°C for a period of 198 hours using the general procedure and giving the results shown in the following Table:

Composition	% Vol. Swell	% Wt. Gain	Hardness (DA)		
			Start	End	Change
1	4.3	2.9	83	85	2
2	3.7	2.6	89	86	-3

The blends showed superior performance.

Example 3

- The procedure of Example 2 was followed except for the following change: composition 1 was exposed to a gaseous mixture of 2,2-dichloro-1,1,1-trifluoroethane (HCFC-123) and anhydrous hydrofluoric acid (AHF) at 120°C for a period of 198 hours.

- O-rings of Composition 1 exhibited a volume swell of only 13.5%, weight gain of only 12.2%, and the initial hardness of 79 increased by a small amount to 82, a change of 3 units.

Example 4

The procedure described in Example 2 was substantially repeated except for the following change: Elastomer O-rings were exposed to gaseous

HCFC-123 cycled at room temperature to 30°C (boiling) temperature for 865 hours.

Composition	% Vol. Swell	% Wt. Gain	Hardness (DA)		
			Start	End	Change
1	1.5	1.1	87	85	-2
2	0.2	0.5	89	85	-4
3	0.7	0.9	88	84	-4
4	2.1	1.6	88	85	-3
5	1.2	0.7	84	85	1
6	2.4	1.7	84	83	-1

- 5 The O-rings of all of these cured compositions exhibited low volume swell, low weight gain and small changes in hardness.

Example 5

- 10 The procedure of Example 2 was substantially followed except for the following change: Elastomer O-rings were exposed to (immersed in) liquid anhydrous HF at 100°C temperature for 170 hours.

Composition	% Vol. Swell	% Wt. Gain	Hardness (DA)		
			Start	End	Change
1	2.5	3.0	85	86	1
2	5.9	4.0	85	87	2

Again, the blends showed superior performance.

15 Example 6

The procedure of Example 2 was substantially repeated except for the following change: Elastomer O-rings were exposed to gaseous hydrochloric acid (HCl) at 120°C temperature for 205 hours.

Composition	% Vol. Swell	% Wt. Gain	Hardness (DA)		
			Start	End	Change
1	1.5	1.5	90	87	-3
2	2.5	1.5	87	85	-2
3	1.8	1.5	83	85	2
4	2.0	1.5	85	86	1
5	2.4	1.7	84	84	0
6	2.5	1.7	87	84	-3

In this test, the blends gave satisfactory performance.

Example 7

- The procedure of Example 2 was followed except for the following change: Elastomer O-rings were exposed to gaseous perchloroethylene (PCE) at 122°C (boiling) temperature for 840 hours.

Composition	% Vol. Swell	% Wt. Gain	Hardness (DA)		
			Start	End	Change
1	5.2	4.2	85	82	-3
2	6.1	4.9	88	84	-4

In this test, the blends gave satisfactory performance.

Example 8

- The following two elastomer blends were fabricated into O-rings as described in the general procedure. Composition 7 was modified from Composition 1 by substituting TFE/PMVE compounded gum which is curable to Kalrez® fluoroelastomer 2035 O-rings for GA-55, and Composition 8 was modified from previous Composition 5 by substituting Viton® B fluoroelastomer for GA-55.

Blend Composition (% by weight)		
	Composition	
Ingredient	7	8
TFE/PMVE	75.00	-
Viton® B	-	50.00
Kel F® 3700	15.92	27.03
Vistalon® 404 EPDM	-	6.76
AC Poly 617A	1.59	-
N-990 Black	6.37	13.51
Halocarbon Oil	0.48	1.01
Diak® #7	0.32	0.68
Luperco® 101XL	0.32	1.01

- These two compounds were then exposed to gaseous HCFC-123 at 35°C boiling temperature at a slightly superatmospheric pressure for a period of 216 hours, otherwise following the procedure of Example 2, giving the
- 5 following results:

Composition	% Vol. Swell	% Wt. Gain	Hardness (DA)		
			Start	End	Change
7	8.3	5.5	98	92	-6
8	15.4	14.1	83	71	-12

Performance of these modified blends was also satisfactory for many applications.

WHAT IS CLAIMED IS:

1. Seal of cured coherent, homogeneous elastomer blend comprising (a) CTFE/VF₂ elastomer, (b) chlorine-free fluoroelastomer, and (c) a minor proportion with respect to the combined weight of (a) and (b) of hydrocarbon polymer.
5
2. Seal of claim 1 wherein said fluoroelastomer is perfluoroelastomer.
3. Seal of claim 1 wherein said elastomer is VF₂/HFP elastomer.
4. Seal of claim 1 wherein said elastomer is TFE elastomer.
- 10 5. Seal of claim 4 wherein said elastomer is TFE/PAVE elastomer.
6. Seal of claim 5 wherein said PAVE is perfluoro(alkoxy alkyl vinyl) ether or PMVE.
7. Seal of claim 1 wherein said blend has volume swell of less than 15%, weight gain of less than 15%, and change in hardness of less than 15 when
15 subjected to the Chemical Process Simulation Exposure Test.
8. Seal of claim 1 wherein the weight proportion of (a) and (b) is 10 to 90 wt% of (a) and complementally to total 100 wt%, 90 to 10 wt% of (b).
9. The seal of claim 1 wherein the amount of hydrocarbon polymer is 1 to 20 wt% based on the combined weight of (a) and (b).
- 20 10. The seal of claim 1 wherein said hydrocarbon polymer is ethylene or propylene polymer.
11. Curable, coherent, homogeneous blend comprising (a) curable CTFE/VF₂ polymer curable to elastomer, (b) chlorine-free fluoroelastomer curable to elastomer, and (c) a minor proportion of hydrocarbon polymer.
- 25 12. Process comprising compounding curable (a) CTFE/VF₂ polymer curable to elastomer, (b) chlorine-free fluoroelastomer curable to elastomer, and (c) hydrocarbon polymer to form a coherent, homogeneous blend thereof.
13. Process of claim 12 and additionally forming said blend into an
30 article and curing said article of said blend.
14. Process of claim 13 wherein said article is a seal or hose.

INTERNATIONAL SEARCH REPORT

Int. Appl. No.

PCT/US 95/06874

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C09K3/10 C08L27/12 //(C08L27/12, 27:12, 23:02)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09K C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US-A-4 948 830 (JON W. MARTIN ET AL.) 14 August 1990 see the whole document ---	1-4, 8-14
A	GB-A-1 120 131 (RAYCHEM LIMITED) 17 July 1968 see page 2, line 22 - line 44; claims; examples 4,5 ---	1
A	DE, A, 21 55 375 (MINNESOTA MINING AND MANUFACTURING CO.) 18 May 1972 see page 5, line 29 - line 33; claims; examples -----	1-13

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. l. Application No

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4948830	14-08-90	NONE	
GB-A-1120131		NONE	
DE-A-2155375	18-05-72	BE-A- 774900	04-05-72
		CA-A- 954648	10-09-74
		FR-A- 2113544	23-06-72
		GB-A- 1354154	05-06-74
		US-A- 3723577	27-03-73